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TRANSACTIONS.

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TRANSACTIONS.

I.—The Activity of Acids as Catalysts in Relation to the Nature of the Solvent Medium.

By HARRY MEDFORTH DAWSON.

IN a previous investigation (Dawson and Wheatley, Trans., 1910, 97, 2048) of the relative rates of tautomeric change of various ketones, in which iodine was used as an indicator of the speed of the reaction, the choice of a solvent for the reacting substances was determined by a preliminary examination of the variation of the rate of change of acetone when the water serving as solvent was gradually replaced by ethyl alcohol. In these experiments, which were made at a temperature of 20°, the concentrations of the acetone and of the sulphuric acid, which was added as a catalyst, were in all cases the same, the experimental data thus indicating directly the changes which are attributable to the variation in the character of the solvent medium. The concentrations of the ketone and the catalyst were, moreover, such that the active mass of the former remained practically constant during the change, whilst the effect of the latter was not altered to any great extent by the hydriodic acid formed as one of the products of the reaction. With increasing proportion of ethyl alcohol in the solvent, the reaction proceeds less completely, but the mechanism of the change is apparently unaltered, for the iodine disappears at a constant speed so long as the amount of iodine present is appreciably in excess of that

depending with the state of equilibrium which is ultimately reached.

The dependence of the reaction-velocity on the composition of the aqueous alcoholic solution is shown by the data in table I, from which it is seen that the velocity is practically the same in water-alcohol mixtures as in pure water, provided that the amount of water present does not fall below about thirty volumes per cent. On further diminution of the water content of the solvent, the velocity increases, and the rate of increase becomes greater as the amount of water present is continuously diminished. The values $k = dx/dt$ are expressed in mols. per litre per minute.

TABLE I.

Acetone, 0.272; Sulphuric Acid, 0.05 mol. per litre.

Grams water per litre of solution	1000	800	600	500	400	300	200	119	48.5	18.5
$k \times 10^6$	23.0	23.0	22.5	22.5	22.0	24.0	25.5	33.0	63	170

On account of the high speed of the reaction, measurements could not be made with sufficient accuracy at 20° in the case of solutions containing less than about one gram-mol. of water per litre, and the investigation of these was carried out at 0° . For these determinations anhydrous alcohol was prepared by Winkler's method (*Ber.*, 1905, **38**, 3612), the material used in the preparation of the anhydrous and moist alcoholic solutions being the product obtained after triple treatment with rasped calcium.

With this anhydrous alcohol, a solution was prepared containing 0.095 mol. of sulphuric acid and approximately 0.05 mol. of iodine per litre. Fifty c.c. of this were introduced into stoppered flasks containing weighed quantities of water, and the volume made up to 100 c.c. with anhydrous alcohol; these solutions were then cooled to 0° , and 2 c.c. of acetone were added to each. Measured volumes of the solutions were then removed from time to time, and the unchanged iodine was titrated, as previously described.

In order to show the course of the reaction in its earlier stages in alcoholic solutions containing little or no water, two experiments are recorded in detail in table II. The measured iodine concentrations in mols. per litre are given under x_1 , and the values calculated from $x_2 = x_0 - kt$ under x_2 .

TABLE II.

(1) Anhydrous Alcohol.

Time (minutes).....	0	15½	23	30	37
$x_1 \times 10^3$	22.45	19.83	18.14	16.90	15.30
$x_2 \times 10^3$	(22.45)	19.51	18.08	16.75	15.42
$k = 0.00019.$					

(2) Alcohol containing 5.02 grams of water per litre.

Time (minutes)	0	20	50	80	110	150
$x_1 \times 10^3$	22.23	21.30	20.32	18.98	17.37	15.54
$x_2 \times 10^3$	(22.23)	21.37	20.08	18.79	17.50	15.78
$k = 0.000043.$						

These data suffice to show that the rate of disappearance of the iodine in anhydrous alcohol and in alcohol containing a small quantity of water is constant, as was previously found for aqueous solutions under similar conditions. From this it seems justifiable to conclude that the mechanism of the reaction under investigation is the same. In table III are given the reaction velocities observed at 0° in two series of experiments exactly similar to those recorded in table II. The solutions were made up as already described.

TABLE III.

Series 1.		Series 2.	
Grams of water per litre.	$k \times 10^6.$	Grams of water per litre.	$k \times 10^6.$
0.0	190	0.0	192
5.0	43	5.1	45
10.1	21	10.0	22
20.0	9	20.1	9

The two series of experiments were quite independent, different samples of anhydrous alcohol being used in the preparation of the two sets of solutions. It is evident that a small quantity of water reduces the speed of the reaction to an enormous extent, the velocity falling to about one-tenth of its value for anhydrous alcohol on the addition of 1 per cent. by volume of water. In view of the sensitiveness of the speed of the reaction towards traces of water, the agreement between the two values for anhydrous alcohol is remarkably good, and affords some guarantee that the alcohol obtained by Winkler's method was really free from water. The above data are not sufficient to show the exact connexion between the speed of the reaction and the water content of the alcoholic solution, but it is evident that for solutions containing from 5 to 20 grams of water per litre, the velocity is approximately inversely proportional to the amount of water present.

The fact that small quantities of water exert a considerable depressing effect on the velocity of chemical change in alcoholic solution is well known, and appears to have been first observed by Goldschmidt in connexion with the process of esterification (*Ber.*, 1895, **28**, 3218; 1896, **29**, 2208; compare also Goldschmidt and Sunde, *ibid.*, 1906, **39**, 711; Goldschmidt and Udby, *Zeitsch.*

physikal. Chem., 1907, **60**, 728; Wegscheider, *Ber.*, 1906, **39**, 1054; Kailan, *Monatsh.*, 1906, **27**, 543 *et seq.*). Other reactions taking place under the influence of acid catalysts are similarly affected, as was found by Bredig and Fraenkel (*Ber.*, 1906, **39**, 1756) in the case of the decomposition of diazoacetic ester in ethyl-alcoholic solution, by Tubandt and Mohs (*Annalen*, 1907, **354**, 259) in the inversion of *l*-menthone in methyl-, ethyl-, and propyl-alcoholic solutions, and by Lapworth and his co-workers (Lapworth and Fitzgerald, *Trans.*, 1908, **93**, 2163; Lapworth, *ibid.*, 2187; Lapworth and Partington, *ibid.*, 1910, **97**, 19) in the conversion of hydrazobenzene into benzidine, the action of bromine on ketones, and the hydrolysis of esters in non-aqueous media. The rate of decomposition of oxalic acid by sulphuric acid was also found by Bredig and Lichty (*Zeitsch. Elektrochem.*, 1906, **12**, 459) to be very much retarded by small amounts of water in excess of that corresponding with the composition H_2SO_4 .

Of these various catalysed reactions, the one for which the influence of water has been examined in greatest detail is the process of esterification in ethyl-alcoholic solution. In regard to the influence of small quantities of water on the velocity of keto \rightarrow enol transformation a few preliminary measurements only have been made in the case of acetone without added solvent in presence of sulphuric acid as catalyst and bromine as indicator (Lapworth, *loc. cit.*, p. 2189).

In the case of the experiments described in this paper, the entire range of alcohol-water mixtures has been examined. To facilitate the comparison of the data obtained at 20° for solutions containing larger quantities of water (table I) with those obtained at 0° for solvents containing relatively little water or none at all (table III), the velocity of the reaction for the solution containing 18.5 grams of water per litre was measured at both temperatures. The speed of the reaction was found to be reduced from $k=170 \times 10^{-6}$ at 20° to $k=13.5 \times 10^{-6}$ at 0° . Assuming that the temperature-coefficient has the same value for a water-free alcoholic solution, and taking into account the small difference between the acid concentrations in the two series of experiments, it is found that the velocity of the reaction in anhydrous alcohol is more than a hundred times (about 115) as great as the velocity in aqueous solution.

The data in table II show that this enormous difference in the rates of change in the two media is not accompanied by any observable difference in the mechanism of the change, for both in aqueous and in alcoholic solution the speed of the reaction is independent of the iodine concentration. The change in velocity is therefore attributable to a difference in the rate of the primary

tautomeric change in the two media, and since this change is catalytically accelerated by acids, the difference in question may be due to a change in the specific reactivity of the acetone or to an alteration in the catalytic activity of the acid.

In reference to this change in activity, experiments were made to determine the influence of the acetone and acid concentrations on the velocity of the reaction in nearly pure alcoholic solutions, previous measurements (Dawson and Leslie, *Trans.*, 1909, **95**, 1860) having shown that the velocity in aqueous solution is proportional to the concentration of the ketone and also to that of the acid. Table IV shows the influence of varying acetone concentration in alcoholic solutions containing 5 and 10 grams of water per litre, the measurements being carried out at 0°.

TABLE IV.

Water, 5 grams per litre; H ₂ SO ₄ , 0.05 mol. per litre.		Water, 10 grams per litre; H ₂ SO ₄ , 0.03 mol. per litre.	
Mols. acetone per litre.	$k \times 10^6$.	Mols. acetone per litre.	$k \times 10^6$.
0.816	150.0	1.36	61.0
0.272	54.0	0.272	12.5
Ratios 3.0	2.8	5.0	4.9

According to these data, the velocity of the reaction in moist alcoholic solution is proportional to the concentration of the ketone. This result is identical with that previously obtained for a pure aqueous solution, and this identity is clearly contradictory to the hypothesis that the large changes in the reaction velocity which are brought about by the addition of small quantities of water to an alcoholic solution are due to the formation of acetone hydrates which are less active than the free acetone or compounds of acetone and alcohol which might be supposed to be present in alcoholic solution. This is evident from a closer inspection of the two experiments made in alcoholic solution containing 10 grams of water per litre. In these the molar ratios of acetone to water are respectively 2.5 and 0.5. If less active hydrated molecules were formed in the moist alcoholic solution, such a variation in the relative quantities of acetone and water should undoubtedly give rise to a velocity ratio much greater than the ratio of the acetone concentrations. Since the velocity and acetone concentration ratios are equal, it follows that the observed variations in the rate of tautomeric change with the nature of the solvent medium are not due to changes in the specific reactivity of the ketone.

The results of measurements of the rate of disappearance of bromine in moist acetone have also led Lapworth to discard hydrate

formation as a possible explanation of the retardation effects. Moreover, determinations of the refractivity and the dielectric constants of acetone-water mixtures (Drude, *Zeitsch. physikal. Chem.*, 1897, **23**, 313; Miss Homfray, *Trans.*, 1905, **87**, 1435) indicate that acetone in aqueous solution does not form hydrates to more than a very small extent.

On the other hand, strong evidence in favour of the view that the variations in the speed of the tautomeric change are due to differences in the activity of the acid catalyst, is afforded by the fact that so many different reactions, in which an acid plays the part of a catalyst, are similarly retarded when small quantities of water are added to the non-aqueous medium in which the reacting substances are dissolved. The view that the anti-catalytic effect of water in these different reactions is not due to any other cause than a change in the availability of the acid is due to Lapworth, and he, in conjunction with his co-workers, has shown that the changes in availability are the same whether measured by changes in esterification velocity or by the amounts of salt which the acid yields in the different moist solutions with a weak monacid base. By mathematical treatment of the conception that the influence of water on acid catalysis is due to a diminution of the quantity of available acid, Lapworth has shown further that this view is in agreement with the generalisations of the ionic theory, and that it can be applied to the facts as readily as the original idea of Arrhenius.

Lapworth's views are obviously opposed to the widely accepted theory that the relative catalytic activities of acids in aqueous solution are determined by the concentration of the "hydrogen" ions, that is to say, the ions which are mainly responsible for the passage of positive electricity through aqueous solutions of acids. The parallelism between the numbers, which represent the relative catalytic activities of the acids on the one hand, and the ionisation coefficients as determined by conductivity measurements on the other, is the main factor which has led to the general adoption of the view that the "hydrogen" ions are the active ions in the two cases. The gradual accumulation of observations, which lend support to the theory that the ions of aqueous solutions are in general hydrated, does not appear to have had any considerable effect on the prevalence of the notion that the electrolytic ions are the catalytic agents.

In particular, this view appears to be adopted by Goldschmidt in a recent summary (*Zeitsch. Elektrochem.*, 1909, **15**, 4) of results obtained in a series of investigations, in which the esterification of various acids in ethyl-alcoholic solution under the influence of

different acid catalysts was examined. The parallelism between the esterification constants and the electrical conductivities for various acids used as catalysts and that between the velocity constants for one and the same acid catalyst at different concentrations and the corresponding ionic concentrations (as measured by the electrical conductivity) are cited as evidence in support of the theory that "hydrogen" ions are the active catalytic agents.

Experiments which were made to ascertain the influence of the concentration of the sulphuric acid as catalyst in the tautomeric transformation of acetone seem to show clearly that this theory is untenable. In these experiments, the concentration of the acetone was 0.272 mol. per litre, and parallel measurements were made with solutions containing respectively 0.15 and 0.03 mol. of sulphuric acid per litre. The experimental data are collected in table V, and, as indicated in the first column, the temperature of comparison was either 20° or 0°, according to the proportion of water in the aqueous alcoholic solvent. The relative speeds of the reaction for a variation in the concentration of the acid in the ratio 5:1 are shown in the fifth column of the table.

TABLE V.

Temperature.	Grams of water per litre of solvent.	$k \cdot 10^6$ for 0.15 molar H_2SO_4 .	$k \cdot 10^6$ for 0.03 molar H_2SO_4 .	Velocity ratio.	Ratio of electrical conductivities.
20°	1000.0	70	14.0	5.0	4.25
20	400.0	73	14.0	5.2	4.8
20	50.0	183	31.0	5.9	3.85
0	10.0	106	12.5	8.5	3.45
0	5.0	225	26.0	8.6	—
0	4.5	238	36.0	8.0	—
0	0.0	920	130.0	7.2	3.55

From the velocity ratios, it is evident that the speed of the reaction is proportional to the concentration of the acid in aqueous solution, and very nearly so in an alcohol-water mixture containing 400 grams of water per litre, but that this is by no means the case in alcoholic solutions which contain little or no water. In anhydrous alcohol, the speed of the reaction becomes more than seven times as great when the concentration of the acid is increased in the ratio of five to one from 0.03 mol. to 0.15 mol. per litre. The inequality in the velocity and concentration ratios is even more pronounced in the case of moist alcoholic solutions, and the series of numbers in the table would seem to show that the divergence is greatest when the alcoholic solvent contains a certain small proportion of water.

With hydrochloric acid as catalyst, a similar lack of proportionality between the speed of the reaction and the concentration

of the catalyst has been already observed for a large number of esterification reactions in moist alcoholic solution (Kailan, *loc. cit.*). In absolute alcohol, on the other hand, it has been found that in many cases the velocity of esterification is proportional to the concentration of the catalyst. This is not, however, always the case, for Kailan has observed that in absolute alcohol the velocity of esterification of the aminobenzoic acids and of 3:5-dinitrobenzoic acid increases more rapidly than the concentration of the catalyst, whilst in the case of 3:4- and 3:5-dihydroxybenzoic acids the velocity increases less rapidly than the concentration of the hydrogen chloride. In the absence of water, the connexion between the activity of the catalyst and its concentration would thus appear to depend on the nature of the catalysed reaction, although in presence of small quantities of water all the available experimental results indicate that the activity of the catalyst increases more rapidly than its concentration.

The difficulty of reconciling these facts with the theory of "hydrogen" ion catalysis has been already pointed out by Kailan and Wegscheider (*loc. cit.*). For sulphuric acid as catalyst, the discrepancy between the catalytic activity and the "hydrogen" ion concentration is shown by a comparison of the velocity ratios in table V with corresponding ratios for the "hydrogen" ion concentration.

To obtain the necessary data, measurements were made of the electrical conductivities of the 0.15 and 0.03 molar solutions of sulphuric acid in various alcohol-water mixtures, and the conductivity ratios thus obtained are recorded in the sixth column of the table.

From the usual ionic point of view, it may be doubted whether the conductivity ratio can be regarded as an exact measure of the "hydrogen" ion ratio, for the conductivity relationships of sulphuric acid in moist alcoholic solutions appear to be of a complex character. On addition of small quantities of water to an alcoholic solution, the conductivity falls very considerably until a minimum is reached; beyond this, further increase in the proportion of water causes the conductivity to rise until in pure water it is about twenty times as large as in anhydrous alcohol. Similar observations have been made by Goldschmidt (*Zeitsch. Elektrochem.*, 1909, 15, 4) in the case of alcoholic solutions of hydrogen chloride, and this behaviour suggests that caution is required in applying the conductivity measurements to the determination of the "hydrogen" ion ratio. In consideration of the small interval of concentration which is involved, it is probable, however, that no serious error will be

committed if the conductivity ratio is taken directly as a measure of the relative "hydrogen" ion concentrations.

Comparing the conductivity ratios with the velocity ratios, it is seen that the values diverge much more in the case of alcoholic solutions which contain little or no water than they do for a pure aqueous solution. Various hypotheses have been advanced to account for such divergences between the catalytic activities and the "hydrogen" ion concentrations in the case of aqueous solutions of acids. An explanation of the very much greater divergences in the use of alcoholic solutions on similar lines seems scarcely possible. On the contrary, the deviations are such that the conclusion seems inevitable that the active catalysts in alcoholic solution are not the ions which are responsible for the electrical conducting power.

In favour of this conclusion is the fact that the catalysing power of sulphuric acid in dilute alcoholic solution is about a hundred times as great as it is in a corresponding aqueous solution, whereas the "hydrogen" ion concentrations appear to be nearly equal. In the case of a 0.05 molar acid, the degree of ionisation in aqueous solution is approximately 0.6, and, according to Kremann and Brassert (*Monatsh.*, 1910, **31**, 195), the degree of ionisation for an alcoholic solution (containing 0.6 per cent. of water) is about 0.5. These data indicate that the concentration of the "hydrogen" ions in aqueous and alcoholic solutions of this order of concentration are approximately the same, whereas the velocity data indicate that the catalytically active component is present in alcoholic solution in very much greater concentration than in a corresponding aqueous solution.

The observed facts are thus seen to be irreconcilable with the assumption that acid catalysis is due to "hydrogen" ions, but, on the other hand, they appear to harmonise with the theory of acid catalysis advanced by Lapworth. According to this, the catalytic activity of an acid is determined by its availability, and if we postulate the existence of free hydrogen ions in solutions of acids, the concentration of these furnishes a measure of the availability. For a given concentration of acid, the proportion of free hydrogen ions is much greater in the case of an alcoholic solution than in that of an aqueous solution, although the concentrations of the positive acid ions—the ethylhydroxonium ions in the one case, and the hydroxonium ions in the other—may be, and probably are, of the same order of magnitude.

The chief results obtained in this investigation may be summarised as follows:

1. Data are recorded showing the influence of the medium on the

rate of tautomeric change of acetone in presence of sulphuric acid as a catalyst for alcohol-water mixtures, ranging from pure water to anhydrous alcohol.

2. In anhydrous alcohol the speed of the reaction is more than a hundred times as great as in water. On addition of small quantities of water to the alcoholic solution, the velocity is greatly diminished.

3. In alcoholic solutions the speed of the reaction is proportional to the concentration of the ketone, but increases much more rapidly than the concentration of the catalyst or the concentration of the "hydrogen" ions.

4. It is shown that the observations are inconsistent with the theory of "hydrogen" ion catalysis, but that they appear to be capable of interpretation on the lines of Lapworth's theory of acids.

For assistance in preliminary experiments, I desire to express my thanks to Mr. R. Wheatley, B.Sc.

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II.—*Cryoscopic, Ebullioscopic, and Association Constants of Trimethylcarbinol.*

By WILLIAM RINGROSE GELSTON ATKINS.

It was suggested by Professor E. A. Werner that trimethylcarbinol might be a useful solvent for molecular-weight determinations by cryoscopy, as it was the only one of the lower alcohols that had a convenient melting point, and was not likely to dissociate completely certain organic compounds which were being studied by him.

As the divergence between the values of E , the molecular lowering of freezing point, as found by experiment and as calculated from the heat of fusion, was very remarkable, the study of the ebullioscopic and association constants was also undertaken.

Trimethylcarbinol was found by Paternò and Ampola (*Gazzetta*, 1897, 27, i, 481) to give one minimum on the freezing-point curve with *p*-bromotoluene, and one with thymol; they point out that the freezing points of these mixtures cannot be even approximately calculated by the formula $E = \frac{RT_0^2}{100s}$. With phenol they find a complex curve, showing two maxima and three minima. Calculation

from their data shows that the compounds $(\text{CH}_3)_3\text{C}\cdot\text{OH}$, $2\text{C}_6\text{H}_5\cdot\text{OH}$ and $3(\text{CH}_3)_3\text{C}\cdot\text{OH}$, $\text{C}_6\text{H}_5\cdot\text{OH}$ are present, making allowance for the flat nature of the curves.

Paternò (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 153) has shown that the compound $(\text{CH}_3)_3\text{C}\cdot\text{OH}$, $2\text{H}_2\text{O}$ exists from a study of the freezing point diagram, but viscosity determinations show that it is completely dissociated a few degrees above the melting point of the pure alcohol. Subsequently, Paternò and Mieli (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 396) drew the conclusion that there was no correlation between the density curve and the temperature-composition curve for the phenol-trimethylcarbinol mixture.

The melting point of the alcohol, $25\cdot53^\circ$, is abnormally high for the series. It seems that this is due to a combination of two factors. It has been pointed out by Carnelley (Smiles, *Chemical Constitution and Some Physical Properties*, p. 200) that among isomerides the compound with the more symmetrical structure possesses the higher melting point, whilst Markownikoff has shown that the compound with the more highly branched chain of carbon atoms melts at the higher temperature. Now trimethylcarbinol is at once the most symmetrical alcohol, for the methyl group ($\text{CH}_3=15$) is very close to the hydroxyl group ($\text{OH}=17$) in weight, and the most highly branched form of carbon atom chain is also present, hence the remarkably high melting point.

Cryoscopic Constant.

Kahlbaum's trimethylcarbinol was purified by distillation with benzene (S. Young, *Fractional Distillation*, p. 233), and placed in the inner tube of a Beckmann apparatus, with stirrer and drying tube attached. The following substances were employed as solutes to determine the constant: *p*-dibromobenzene, acetanilide, thiocarbamide, *p*-toluidine, and α -naphthylamine. The details are given in the experimental part of the paper. The values of E ranged from 134.5 to 82.5 for *p*-dibromobenzene as the concentration increased, from 154.4 to 72.9 for acetanilide, from 152.5 to 137.4 for α -naphthylamine, whilst thiocarbamide gave $E=83.7$. Taking de Forcrand's (*Compt. rend.*, 1903, **136**, 1034) value for the latent heat of fusion, $s=20\cdot978$ cal., and evaluating the expression $E=\frac{RT_0^2}{100s}$,

where $R=1\cdot991$ cal. and T_0 is the melting point on the absolute scale, it is found that E (calc.) = 84.5.

It appears at first sight as if the determinations had been made with substances which dissociated in solution, and thus gave in dilute solutions a depression nearly twice as great as would be

expected, whilst in concentrated solutions the theoretical value was more nearly approached. However, the chemical evidence is strongly against the dissociation of the solutes employed to anything like the extent required, at any rate. Moreover, it was found that the pure alcohol was practically a non-conductor, and when a little *p*-toluidine was dissolved in it, no difference could be detected in its conductivity, although a sensitive galvanometer was used.

To test the possibility of the unexpectedly great lowering of the freezing point being due to the hygroscopic nature of the liquid, the apparatus was allowed to remain for one day, when the depression was found to be only 0.02° lower than on the previous day. Taking into account the difficulty of obtaining two consecutive readings with this solvent, which differ by less than 0.01° , it is clear that the slow absorption of water will not explain the results. The decrease in E with increase in concentration is also against such an explanation. Separation of the solute with the solvent would, of course, lower the value of E , and so need not be considered further.

There still remains the possibility of error having arisen through the too great separation of the solvent on freezing, and through a radiation effect from the cooling bath. Accordingly, fresh determinations were made, using *p*-dibromobenzene as solute, the temperature of the bath being -0.8° and -2.5° below that of the solution. The value thus obtained for Δ was corrected by Raoult's equation (*Compt. rend.*, 1897, **125**, 751), $\Delta = \Delta_{(\text{obs.})}(1 - KS)$, where S is the supercooling in degrees, and K is a constant obtained from the expression:

$$K = \frac{1}{L} \left(1 + \frac{r}{R} \right) \pm \left(1 + \frac{r}{R} \right) \frac{t}{T} \times \frac{1}{SL},$$

in which L is the heat of fusion of the solvent, r the water equivalent of the part of the apparatus wetted, R the water equivalent of the solvent used, t the time from freezing to steady temperature, and T the time for the apparatus to cool or warm 1° by radiation. The resultant value was $E=128$, which agrees well with the determinations of E in the main series.

Thus for a dilute solution of *p*-dibromobenzene the value of E is 128, whereas theory requires it to be 84.5. The discrepancy must be accepted as a fact, and an explanation attempted. On this basis the nearly normal values obtained with more concentrated solutions are to be accounted for as due to association of the solutes, which is just what is to be expected, especially with substances containing amino-groups. *p*-Dibromobenzene was selected as a solute as being in every way a "normal" substance, giving a unimolecular liquid on fusion (*Crompton, Trans.*, 1897, **71**, 925). Accordingly, the

value for E found with it has been taken in preference to a mean value.

It is of interest to calculate the values of E from data given by Paternò (*loc. cit.*) for the alcohol-water concentration-temperature diagram. Here $E=88.8$ for an addition of 1.34 per cent. of water, but falls off considerably, due no doubt to association of the water. With 5.74 per cent. of water, $E=64.6$, and at the minimum point of the curve, $E=45.1$. As the depression of freezing point amounts to 6.6° for 1.34 per cent., it is probable that a higher value for E would be arrived at for smaller depressions. Considering the other end of his curve, in which water is the solvent, with 5.79 per cent. of alcohol, we obtain $E=19.1$, and with 11.19 per cent., $E=25.1$. The molecular weight of the alcohol, of course, varies in the inverse direction. Taking $E=18.7$ for water, then $M=72$ and 55 at the respective concentrations. Even allowing for the calculations being made on a percentage basis, not as grams per 100 grams, the results would appear to indicate dissociation of the alcohol, an appearance quite comparable with the behaviour of certain substances in the alcohol as solvent.

If, however, with Crompton (*loc. cit.*), we admit that the association of the solvent has to be taken into account as well as that of the solute, we have to consider his third case, that of a unimolecular solute in an associated solvent, and must calculate

$Pv = RT \times \frac{x}{a}$, and $E = \frac{RT^2_0}{100s} \times \frac{x}{a}$, where " a " is the association factor

of the vapour, " x " the association factor of the liquid, and s and R denote the heat of fusion and gas constant in calories. Then, as $a=1$ and $x=1.9$ from $26-36^\circ$, as found by Ramsay and Shields' method (Carrara and Ferrari, *Gazzetta*, 1906, **36**, i, 419):

$$E = \frac{1.991T^2}{100s} \times \frac{1.9}{1.0} = 160.5.$$

This value for E is sufficiently high to include all the values found by experiment, the lower values being, as before, attributed to association of the solute. As, however, the above relation of Crompton has been rejected (Nernst, *Theoretical Chemistry*, Eng. Trans., 4th ed., p. 268), this explanation can hardly be regarded as satisfactory.

Turning now to van't Hoff's equation, $E = \frac{RT^2}{100s}$, it is seen that s is the only value open to question. Taking the experimentally found value, $E=128$, and using it to calculate s , we obtain $s=13.84$ cal., as against 20.98 cal. (de Forcrand, *loc. cit.*). De Forcrand had doubts as to whether the definite state of the solid was reached at once. If it is not, different values would, of course, be found

according to the length of time the alcohol remained solid. He determined C_s between -21.5° and $+14^\circ$, and concludes that it only increases between his first determination and his last by 1 per cent. at the most. Hence s cannot change either. In his first experiment, however, the alcohol was kept at -21.5° for four hours. Thus a quick change would escape detection by his method, the very low temperature conducing to even greater rapidity. He proceeds further to test his values by the relation he had previously developed,

$$\frac{L+S}{T} = 30 \text{ (28 to 32) (} \textit{Compt. rend.}, 1903, \textbf{136}, 945),$$

where T is the

absolute boiling point, and L and S are the molecular heats, of vaporisation at the boiling point and of fusion respectively. Then

$$\frac{L+S}{T} = \frac{9428+1948}{355.8} = 30.85, \text{ the agreement being satisfactory.}$$

If a similar calculation be made, using $s=13.84$ and consequently

$$S=1024, \text{ we obtain } \frac{9426+1024}{355.8} = 29.66, \text{ which is still within the}$$

limits of the constant.

The abnormally low value of Crompton's relation (*loc. cit.*),

$$\frac{10sd}{T} = 1.00 \text{ (where } d \text{ is the density at the melting point, which is}$$

represented by T on the absolute scale), which trimethylcarbinol affords, namely, 0.54, may point to 20.98 being too low a value for s , but it seems far more likely that it is due to the remarkably high value of T , due to the influences referred to before.

Now it is quite possible that in the case of trimethylcarbinol we are dealing with a substance possessing two crystalline modifications, the unstable rapidly passing into the stable. Indeed, a number of facts seems to point to this conclusion. To begin with, when the alcohol is supercooled and suddenly solidifies, a felted mass of needle crystals is produced. After keeping for a day at 22° , none of this form can be found, but a number of plate-like forms have appeared, which are often hexagonal in shape. In fact, in two or three hours but few of the needle form are to be seen. Both forms illuminate and are extinguished when rotated on the stage of a microscope in plane-polarised light. The minute needles and the longer ones formed more slowly give greys of the first order, as do the smaller plates, whilst the larger ones give all colours. De Forcrand (*loc. cit.*) describes the crystals as derived from a flattened orthorhombic prism with modifications h' . He does not mention the needle form. Professor J. Joly very kindly examined both forms for me, and, while agreeing that the large crystals were orthorhombic, did not think it possible to assert to what system the needles belonged. In the crystallisation of

naturally occurring minerals, monoclinic substances very frequently assume an acicular form, and most organic compounds belong to this system, but, on the other hand, the birefringence of both plates and needles was very much the same. To sum up, examination of the crystals in polarised light gives no certain evidence for or against the existence of two modifications.

An attempt was made to study the change by taking a series of photographs under polarised light, as described by Pope (*Trans.*, 1899, **65**, 455) in his work on chloral hydrate. However, owing to the difficulty of preventing the crystals from melting without a deposit of dew on the slide, I have not as yet been able to obtain good photographs.

It may be thought that in the passage from one crystalline condition to another the change in the heats of fusion would not be at all so great as from 13.84 cal. to 20.98 cal., for in the case of rhombic and monoclinic sulphur the difference is small. With chloral hydrate, however, Berthelot (*Compt. rend.*, 1880, **90**, 842, 1511) found $s=17.52$ cal. for the freshly melted crystals, and $s=33.23$ for those which had remained solid for some time. Pope subsequently proved that chloral hydrate was polymorphic, and quite a number of substances show these phenomena in a lesser degree.

That the discrepancy in the two heats of fusion of trimethylcarbinol is due to the existence of two crystalline modifications, one very unstable, seemed to me to be all the more probable, as Tammann (*Ann. Phys. Chem.*, 1899, [iii], **68**, 553, 629) has found a triple point for the liquid and two solid phases at 60° and 1700 kilograms pressure. From the triple point, two melting-point curves branch, and also a transition curve, giving the temperatures and pressures at which the modifications change in the solid state. From a study of crystals which are absolutely stable only under high pressures, Skrabal (*Zeitsch. physikal. Chem.*, 1910, **73**, 171) points out that there is a connexion between the velocity of a change and the stability of the reaction products in such a way that the more rapid the reaction the greater is the possibility of obtaining the less stable products. This, he states, is in accord with the results of direct experiment. Now, the separation of the needle crystals of trimethylcarbinol is very rapid, and it seems probable that this is the form which Tammann found to be stable only at high pressures and temperatures. Its great instability at the ordinary temperature under atmospheric pressure accounts for its rapid disappearance, and also shows why the heat of fusion of the two forms is so different.

Ebullioscopic Constant.

Taking the mean of values obtained with *p*-dibromobenzene, carbamide, and naphthalene, the constant is found to have the value $E=17.45$. Lower values, $E=13.77$ and $E=13.17$, were obtained with thiocarbamide and stearic acid respectively. Calculation from van't Hoff's equation gives $E=19.78$.

D. E. Tsakalotos (*Compt. rend.*, 1907, **144**, 1104) gives the relation:

$$E = M \times \frac{1}{\frac{475 \log T'}{T'} - 0.35},$$

where T' is the absolute boiling point. This gives $E=19.17$, the agreement with van't Hoff's equation being good. As, however, an associated liquid is being considered, the expression $\frac{E}{E_x} = \frac{MT}{M_1 T_1}$ should be used, where E is the value for another member of the homologous series considered. Taking $E=11.5$ for ethyl alcohol, the value of E_x is 18.97. This is in closer agreement with the experimentally determined value.

Baume and Tsakalotos (*Compt. rend.*, 1907, **144**, 373) give the equation $L = \frac{RT^2}{JMp} \frac{dp}{dT'}$, where J is the mechanical equivalent of heat.

and R is the gas constant. Combining this with $L = \frac{0.02T^2}{E}$ gives $\frac{dp}{dT'} = \frac{0.01Mp}{E}$, taking $\frac{R}{J} = 2$.

Not being able to find a recorded value for $\frac{dp}{dT'}$ for trimethylcarbinol, that for propyl alcohol was taken, $\frac{dp}{dT'} = 28.8$. The above equation gives $E=19.53$, in very close proximity to the previous values.

If, on the other hand, the value of E from van't Hoff's equation be taken, calculation gives $\frac{dp}{dT'} = 28.4$ for the tertiary alcohol.

To sum up we have:

Experimental.	van't Hoff (calc.).	Tsakalotos (calc.).	Baume and Tsakalotos (calc.)
E 17.45	19.78	19.17 and 18.97	19.53

It thus appears that the experimental value is too low for some reason. Further determinations are desirable.

De Forcrand's value for L was employed. In his work, $\frac{L}{T'} = \frac{9426}{355.8}$ is given as 22.49, evidently a misprint for 26.5, which is close to the value given by the other alcohols.

Association Factor.

The calculation was made from Ramsay and Shields' formula from values of γ_t recorded in the experimental portion of the paper. The values of Carrara and Ferrari (*loc. cit.*), with which I subsequently became acquainted, are given for comparison; x denotes the association factor, t represents the range of temperature.

t .	x .	t .	x (Carrara).
34.5—46.4°	1.406	26—36°	1.934
34.7—46.6	1.370	36—40	1.515
46.4—80.0	1.295	40—45	1.268
46.6—79.5	1.313	Mean 36—45	1.391
Mean 35.0—47.0	1.388		

The agreement between the two sets of values is satisfactory. The high value of x at the lower temperatures is to be noted. It is of interest to compare these values with those arrived at by Walden's equations (*Zeitsch. physikal. Chem.*, 1908, 65, 129). He gives $\frac{\lambda_s}{\alpha_s^2} = \text{const.} = 17.9$, where λ_s denotes the latent heat of evaporation at the boiling point, and α_s^2 is the specific cohesion at the same temperature. Here $\alpha_s^2 = \frac{2\gamma}{g\rho}$.

Calculation shows some abnormality, for trimethylcarbinol gives $\text{const.} = 24.8$. Again, he gives $\frac{Ma_s^2}{T_s} = 1.16$, and the divergence of this constant from its normal value may be taken as a measure of the association. The calculated constant is 1.06, which gives $x = 1.094$ at the boiling point.

Dutoit and Mojoiu (*J. Chim. phys.*, 1909, 7, 169) have shown that $\frac{\lambda_s}{\alpha_s^2}$ is approximately constant, varying from 0.0173 to 0.0188, whereas $\frac{ML}{\gamma(Mv)^{\frac{2}{3}}}$ varies from 0.0163 to 0.0205. They apparently take $\alpha_s^2 = \frac{2\gamma}{\rho}$. Calculating thus, the tertiary alcohol gives $\frac{\lambda_s}{\alpha_s^2} = 0.0253$, a considerable divergence.

Longuinescu has studied association by a different method (*J. Chim. phys.*, 1908, 6, 552). He finds for unassociated liquids that the following relation holds: $\left(\frac{T}{100D_0}\right)^2 = n$, where n is the number of atoms in the molecule. By a comparison of n (calc.) with n (theory), the degree of association may be estimated. Taking Paternò's value for D_0 , trimethylcarbinol gives $n = 19.1$ (calc.), $n = 15$ (theory); hence at 0°, $x = 1.27$, which does not agree with the results of the other methods. As it might not be permissible to use this value for D_0 ,

since the melting point is 25.43° , the constant was calculated for pentane and hexane, as being in every way normal liquids, at 30° , taking the densities given by Young (*Sci. Proc. Roy. Dublin Soc.*, 1910, **12**, No. 31). Then for $\frac{T'}{D\sqrt{n}} = \frac{T'}{D'\sqrt{n'}} = 100$ (approx.) the

values 121.5 and 117.5 were obtained for pentane and hexane respectively at 30° , also 116.2 and 113.0 at 0° . Substituting the mean constant at 30° , and correcting for the constant at 0° being 114.6 instead of 100, the value $x = 1.12$ at 30° is obtained. The agreement is no better than before. To sum up, the values arrived at by Ramsay and Shields' method agree fairly with that found by Walden's equation for the boiling-point temperature. It will be noticed that the former measurements give the mean value over a range of temperature, whilst the latter give the value at a definite temperature. The results obtained by Longuinescu's relation do not agree with those of the two previous methods, and judging by the wide divergence of the constant even with normal liquids, such as pentane and hexane, but little more than qualitative results can be obtained from this method.

EXPERIMENTAL.

Cryoscopic Constant.

The apparatus used was the ordinary Beckmann, with a very wide air space between the freezing tube and the outer jacket, which was also an air space, as the freezing point of the alcohol was only slightly above room temperature. When the solvent was supercooled 0.3° to 0.6° , the appearance of needle crystals was extremely rapid, and the temperature rose. A steady state was soon reached, but as a considerable quantity of the solvent had crystallised out, the tube was withdrawn, and the heat of the hand sufficed to melt most of the crystals. The tube was then replaced and allowed to steady down. It reached a point 0.04° to 0.05° above the former reading. This was taken as the true freezing point. It is worthy of note that this is close to the correction calculated from Raoult's formula and applied in the last experiment.

The alcohol used all distilled over between 82.35° and 82.55° under 760 mm. pressure (corr.). In the tables below, s denotes the weight of solute dissolved in 100 grams of solvent; Δ the depression of freezing point; E the molecular lowering constant as calculated from Δ ; and M the molecular weight of the solute as calculated from Δ and the value of E obtained from van't Hoff's formula (namely, 84.5); t denotes the temperature of the outer air jacket, the inner air jacket being about 0.7° higher. From 10 to 12 grams of alcohol were used in each experiment.

Solute: *p*-dibromobenzene, $M = 236$.

<i>s.</i>	Δ .	<i>E.</i>	<i>M.</i>	<i>t.</i>
2.27	1.18	122.8	163	19.6°
5.42	2.31	100.5	198	21.1
8.99	3.14	82.5	242	—
10.83	(3.61)	—	—	19.9

Fine crystals of the solute separated before the solvent froze.

0.31	0.17	128.0	155	19.7°
1.04	0.47	106.6	187	—

Solute: acetanilide, $M = 135$.

Solvent contained about 1 per cent. of *p*-dibromobenzene.

<i>s.</i>	Δ .	<i>E.</i>	<i>M.</i>	<i>t.</i>
0.38	0.43	154.4	75	19.1°
1.15	0.97	112.3	100	—
1.93	1.47	102.6	111	—
6.31	3.41	72.9	156	—

Solute: thiocarbamide, $M = 76$.

<i>s.</i>	Δ .	<i>E.</i>	<i>M.</i>	<i>t.</i>
0.33	0.465	83.7	61	18.9°

Solute: *p*-toluidine, $M = 107$.

<i>s.</i>	Δ .	<i>E.</i>	<i>M.</i>	<i>t.</i>
0.27	0.37	147.7	61.7	21.0°
0.46	0.65	152.5	59.3	—
0.78	1.07	147.2	61.4	—
1.93	2.50	138.6	65.3	—
3.26	4.19	137.4	65.8	—

Solute: α -naphthylamine, $M = 143$.

<i>s.</i>	Δ .	<i>E.</i>	<i>M.</i>	<i>t.</i>
0.31	0.247	112.1	108.6	21.7°
0.66	0.54	116.9	103.4	—
1.16	0.89	109.8	110.0	—
2.10	1.41	95.8	126.1	—
4.05	2.43	85.7	141.0	—
6.71	3.73	79.4	152.2	—

Solute: water, $M = 18$. From Paternò's curve data.

H ₂ O per cent.	Δ .	<i>E.</i>	<i>M.</i>
1.34	6.6	88.8	17.1
2.53	12.2	86.8	17.5
3.64	15.3	75.5	20.0
4.55	18.0	67.3	21.3
5.74	20.6	64.6	23.5
8.00	25.4	57.0	26.7
12.03	30.2 (max. Δ)	45.1	33.6

Solute: trimethylcarbinol, $M=74$. Water as solvent.

From Paternò's curve data.

Alcohol per cent.	Δ .	E .	M .
5.79	1.5	19.2	72
7.74	2.4	23.0	61
11.19	3.8	25.1	55

Revision Series.

Solute: *p*-dibromobenzene, $M=236$.

<i>s</i> .	Δ .	E .	M .	<i>t</i> .
0.295	0.167	133.6	149.4	0.8° below m. p. of alcohol
1.91	{ 1.12 (obs.)	—	145.0	} 2.8° below m. p. of alcohol
	{ 1.04 (corr.)	128.1	155.6	

The correction was made from Raoult's equation,

$$\Delta = \Delta_{(\text{obs.})} (1 - KS),$$

where

$$K = \frac{1}{L} \left(1 + \frac{r}{R} \right) \pm \left(1 + \frac{r}{R} \right) \frac{t}{T} \times \frac{1}{SL}.$$

(The notation has been previously explained.)

The second term is negligible, as $t=1$ min., $T=20$ min., and $S=0.08^\circ$. However, as $r=14.1$, and $R=14.58 \times 0.722$, the correction as a whole is considerable.

Constants of trimethylcarbinol employed in calculations throughout the paper:

Melting point 25.53° , and boiling point 82.55° (S. Young, *Fractional Distillation*).

Melting point 25.43° , and boiling point 82.8° , at 761 mm. pressure. (De Forcrand.)

Sp. heat, liquid, $C_l = 0.722$ from 25.45° to 44.80° . (De Forcrand.)

Sp. heat, solid, $C_s = 0.580$ from -21.5° to $+14^\circ$. (De Forcrand.)

Heat of fusion, $s = 20.978$ cal.

Molecular heat of fusion, $S = 1552$ cal. } At 25.45° . (De Forcrand.)

Heat of vaporisation, $l = 127.38$ cal.

Molecular heat of vaporisation, $L = 9426$ cal. } At 82.8° .

(De Forcrand, *loc. cit.*)

$\rho_4^t = 0.81388 - 0.001256t$ (Paternò, *Atti R. Accad. Lincei*, 1907, [v], 16, ii, 153). Paternò actually gives $0.0001256t$, but I believe this to be a misprint, as it does not agree with his own values for ρ_4^t , or with the values of Thorpe and Jones (*Trans.*, 1893, 63, 278).

Ebullioscopic Constant.

The apparatus used had a platinum wire fused in the bottom, and was surrounded by a vapour jacket. This was filled with pure

benzene, the boiling point of which differs only by 2.5° from that of the alcohol. There was not enough of the pure alcohol to use as a jacket. A series of readings was taken in each case, and chips of a clay pipe stem were added from time to time to avoid superheating. The stem had been boiled with water after being broken up, and was heated to redness and allowed to cool, just before use.

Solute: *p*-dibromobenzene, $M=236$.

<i>s.</i>	Δ .	<i>E.</i>
2.01	0.122	14.31
5.81	0.371	15.05
8.27	0.578	16.50
11.67	0.850	17.21

Solute: thiocarbamide, $M=76$.

<i>s.</i>	Δ .	<i>E.</i>
0.81	0.140	13.14
1.18	0.213	13.77

Solute: carbamide, $M=60$, in presence of the thiocarbamide of the previous series.

<i>s.</i>	Δ .	<i>E.</i>
0.695	0.205	17.69
2.07	0.596	17.24

Solute: stearic acid, $M=284$, in presence of carbamide and thiocarbamide, as before.

<i>s.</i>	Δ .	<i>E.</i>
1.13	0.049	12.50
3.05	0.178	13.17

Solute: naphthalene, $M=128$, in presence of thiocarbamide, carbamide, and stearic acid, as before.

<i>s.</i>	Δ .	<i>E.</i>
1.87	0.150	17.66

Calculation from $E = \frac{RT^2}{100l}$ gives the value 19.78 as against 17.45,

a mean of the values obtained for carbamide, naphthalene, and the highest value for *p*-dibromobenzene. It will be noticed that there is a rise in the value of *E* with rise in concentration, which is the very reverse of the effect of association. This is most marked in the *p*-dibromobenzene series, and is quite beyond the range of experimental error in determining the boiling point. The question

needs further investigation, but it seems possible that it may be explained by the adsorption of the solute by the pipeclay chips, which were present in quantity.

Association Factor.

The value of γ was ascertained by measuring the height of the liquid in a capillary tube at various temperatures, using pure ethyl ether, carbon disulphide, and benzene to give constant temperature vapour jackets. A thermometer capillary was used, after its uniformity of bore had been tested. All measurements were made on a falling column. Before taking a reading, the temperature was maintained constant to 0.05° for fifteen to twenty minutes. In the tables, h denotes the height in scale divisions, one division = 0.0798 cm. Radius of tube = 0.0096 cm., as found by calibration with mercury.

Series A.

The melting point of the alcohol used was 23.95 ; $\rho_{\frac{25}{4}} = 0.7829$; from this, $\rho_4^0 = 0.8143$ was found by Paternò's formula, and the other values were calculated by it from the above value.

h_t	ρ_t	t	γ_t in dynes.
68.1	0.7705	34.5	19.45
65.1	0.7556	46.4	18.23
56.1	0.7133	80.0	17.84
—	0.7103	82.5	17.81 (calc.).

Series B.

The alcohol employed distilled over between 82.51° and 82.55° under 770 mm. pressure (corr.).

h_t	ρ_t	t	γ_t
67.9	0.7703	34.7	19.38
64.9	0.7553	46.6	18.17
56.0	0.7140	79.5	17.82
—	0.7103	82.5	17.79 (calc.).

From these values, the association factor x was calculated, employing the expression:

$$Mx = \left\{ \frac{-2.12(t_0 - t_1)}{\gamma_0 v_0^{\frac{2}{3}} - \gamma_1 v_1^{\frac{2}{3}}} \right\}^{\frac{2}{3}}$$

The values of γ at the boiling point 82.5° were calculated by means of the coefficients 0.012 and 0.011 for the change in the value of γ expressed in dynes per degree in series A and B respectively. These were derived from the 46— 80° range. The surface-tension measurements were performed in the presence of dry air, not in a

vacuum. That this is quite permissible has been shown by Renard and Guye (*J. Chim. phys.*, 1907, 5, 81).

I take this opportunity of expressing my thanks to Professor S. Young for the use of apparatus and for the benefit of his advice.

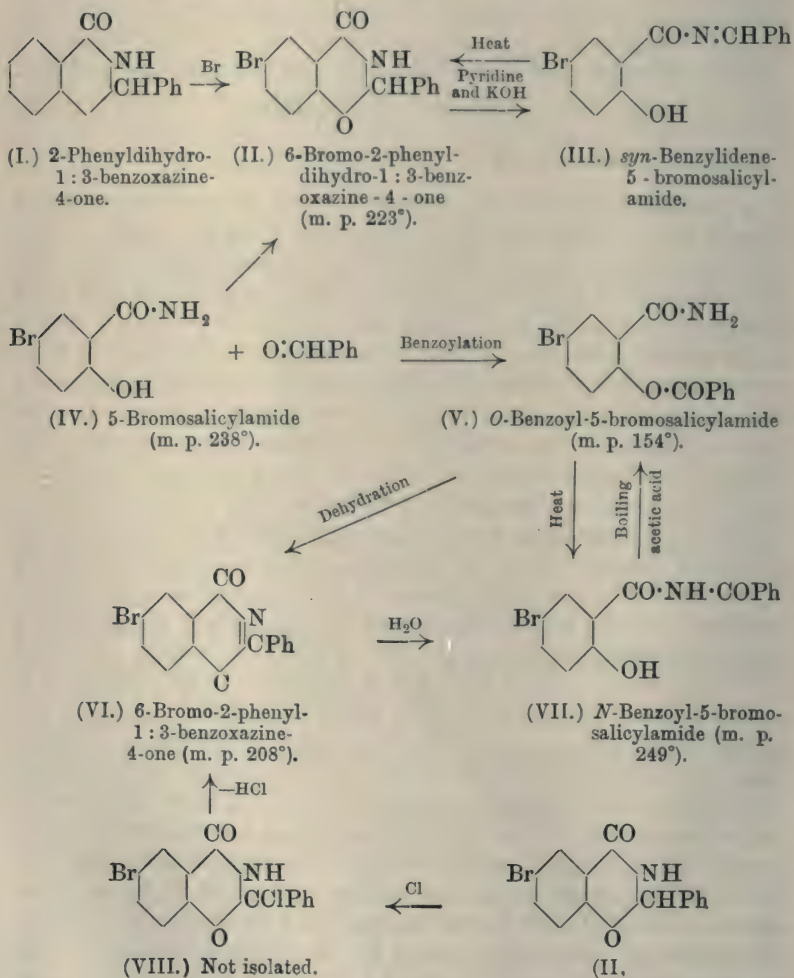
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III.—6-Bromo-2-phenyldihydro-1:3-benzoxazine-4-one and Related Derivatives.

By ERNEST CHISLETT HUGHES and ARTHUR WALSH TITHERLEY.

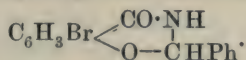
IN a previous paper (*Trans.*, 1910, **97**, 1368) the authors described a series of chloro-derivatives in connexion with the study of the action of chlorine on 2-phenyldihydro-1:3-benzoxazine-4-one (I). The behaviour of the latter compound with bromine has now been examined, and it has been found that simple bromination occurs in the benzene nucleus, yielding 6-bromo-2-phenyldihydro-1:3-benzoxazine-4-one (II), whilst no substitution of the 2-hydrogen atom takes place such as occurs in the corresponding experiments with chlorine; that is, the expected unsaturated derivative, 6-bromo-2-phenyl-1:3-benzoxazine-4-one (VI), is not produced. This compound, however, can be obtained by submitting 6-bromo-2-phenyldihydro-1:3-benzoxazine-4-one (II) to the action of chlorine instead of to the further action of bromine, when in benzotrichloride solution at 110° substitution occurs at position 2, yielding the intermediate 2-chloro-6-bromo-derivative (VIII), which immediately loses hydrogen chloride as in the case of the 2:6-dichloro-compound (*loc. cit.*). It is evident that the hydrogen atom at position 2 is readily affected by chlorine, but not by bromine. Further, the unsaturated ring compound (VI) has been synthetically prepared from *O*-benzoyl-5-bromosalicylamide (V) (obtained by pyridine benzylation of 5-bromosalicylamide, IV) by the same dehydration method as that used in the preparation of the corresponding 6-chloro-compound. Further, the constitution of the dihydro-compound (II) has been confirmed by its independent synthesis from 5-bromosalicylamide (IV) and benzaldehyde. The properties of the two bromo-oxazone compounds (II and VI) are in every respect similar to those of the corresponding chloro-derivatives, and whilst 6-bromo-2-phenyldihydro-1:3-benzoxazine-4-one (II) on treatment with

pyridine and alkali yields a labile *syn*-benzylidene-5-bromosalicylamide (III), and with boiling dilute alkali, benzaldehyde and 5-bromosalicylamide, 6-bromo-2-phenyl-1:3-benzoxazine-4-one (VI) is converted by treatment with alkali (or acid) into *N*-benzoyl-5-bromosalicylamide (VII), which on further hydrolysis gives 5-bromosalicylamide and benzoic acid. The same reversible rearrangement phenomena have been observed between *O*- and *N*-benzoyl-5-bromosalicylamides (V and VII) as between the corresponding 5-chloro-derivatives and *O*- and *N*-benzoylsalicylamides. The above relations are expressed in the scheme:



EXPERIMENTAL.

6-Bromo-2-phenyldihydro-1: 3-benzoxazine-4-one,



(1) *Bromination of 2-Phenyldihydro-1: 3-benzoxazine-4-one.*—Bromination proceeds easily in the cold, but owing to a secondary reaction, in which some water appears to be produced, a considerable quantity of bromosalicylamide and benzaldehyde is formed as a by-product. A solution of 10 grams of 2-phenyldihydro-1: 3-benzoxazine-4-one in chloroform was gradually treated with 5.2 grams of bromine; the red colour rapidly disappeared, and a pale yellow solid separated (4.5 grams), which, after two hours, was collected and recrystallised from alcohol. It melted at 235°, gave a strong violet colour with ferric chloride, dissolved with slight fluorescence in sodium hydroxide, and was identified as 5-bromosalicylamide. (Found, N=6.45; Br.=36.68. Calc., N=6.48; Br=37.03 per cent.)

From the chloroform filtrate, which contained impure benzaldehyde, 6-bromo-2-phenyldihydro-1: 3-benzoxazine-4-one (4.6 grams) was isolated as a pale yellow solid by evaporation and digestion with cold dilute sodium hydroxide. It was obtained pure, by recrystallisation from hot benzene, in fine, colourless needles, melting at 223°:

0.3506, by Kjeldahl's method, required 11.2 c.c. *N*/10-HCl. N=4.42. 0.2186 gave 0.1340 AgBr. Br=26.08.

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{NBr}$ requires N=4.61; Br=26.31 per cent.

The compound is sparingly soluble in cold alcohol, benzene, or acetone, moderately so in cold chloroform, and readily soluble in hot alcohol or benzene, from both of which it crystallises well on cooling. It is readily decomposed on warming with dilute sodium hydroxide, giving benzaldehyde.

(2) *Condensation of 5-Bromosalicylamide and Benzaldehyde.*—The requisite 5-bromosalicylamide (described by Kauschke, *J. pr. Chem.*, 1895, [ii], 51, 211) was obtained by adding 60 grams of bromine gradually to a boiling solution of 50 grams of salicylamide in 1500 c.c. of chloroform. A vigorous reaction took place, the colour of the bromine disappearing immediately, and a copious precipitate of the bromo-derivative being formed. The chloroform was finally distilled off in order to remove the hydrogen bromide, which proved troublesome unless eliminated at this stage, and the solid collected and washed with a little ether. After recrystallisation from alcohol, it melted at 238° (Kauschke gives 232°). The condensation of 5-bromosalicylamide and benzaldehyde was easily

effected. Five grams of bromosalicylamide were dissolved by warming in 20 c.c. of benzaldehyde, and 0.5 c.c. of alcoholic hydrogen chloride added. After heating at 100° for a few minutes and allowing to cool slowly, 6-bromo-2-phenyldihydro-1:3-benzoxazine-4-one separated, practically pure, as a thick mass of colourless crystals (6 grams), which were collected and washed with a little alcohol and ether. It melted at 219°, and, after recrystallisation from alcohol, at 223°. The substance was identical in every respect with that obtained by the bromination method, and a mixture of the two melted at 223°:

0.4666, by Kjeldahl's method, required 15.5 c.c. *N*/10-HCl. *N*=4.64. 0.4104 gave 0.2540 AgBr. Br=26.34.

$C_{14}H_{10}O_2NBr$ requires *N*=4.61; Br=26.31 per cent.

syn-Benzylidene-5-bromosalicylamide, $C_6H_3Br \begin{matrix} \text{CO} \cdot N : CHPh \\ | \\ OH \end{matrix}$.

Two grams of 6-bromo-2-phenyldihydro-1:3-benzoxazine-4-one in 30 grams of pyridine were shaken with 20 c.c. of 10 per cent. sodium hydroxide for half an hour, after which time the bright yellow colour first produced had disappeared. The solution was diluted with water to 750 c.c., and acidified at 0° with dilute hydrochloric acid. The resulting thick, white, amorphous precipitate, consisting of the *syn*-bromo-derivative, was collected, repeatedly washed with water, and dried on porous porcelain in a vacuum. The melting point (100—150°) was indefinite, and it was not found possible to crystallise the compound without rearrangement to the cyclic isomeride, but it was practically pure, as shown by its properties and analysis. The yield was quantitative:

0.5166, by Kjeldahl's method, required 17.2 c.c. *N*/10-HCl. *N*=4.66. 0.1952 gave 0.1238 AgBr. Br=26.67.

$C_{14}H_{10}O_2NBr$ requires *N*=4.61; Br=26.31 per cent.

syn-Benzylidene-5-bromosalicylamide is very sparingly soluble in solvents in the cold, whilst in the hot it rearranges. On melting, it also rearranges in the course of about forty-five seconds to 6-bromo-2-phenyldihydro-1:3-benzoxazine-4-one, which solidifies in the tube, and then melts at 219—220°.

6-Bromo-2-phenyl-1:3-benzoxazine-4-one, $C_6H_3Br \begin{matrix} \text{CO} \cdot N \\ || \\ O - CPh \end{matrix}$.

1. Preparation from 6-Bromo-2-phenyldihydro-1:3-benzoxazine-4-one.

The action of bromine on 6-bromo-2-phenyldihydro-1:3-benzoxazine-4-one was examined under a variety of conditions, but in

no case could the desired 6-bromo-2-phenyl-1 : 3-benzoxazine-4-one be isolated. The action in all cases led to fission of the ring, with production of 5-bromosalicylamide. Chlorine, however, gave the desired result. Eight grams of 6-bromo-2-phenyldihydro-1 : 3-benzoxazine-4-one, dissolved in the minimum quantity of benzotrichloride at 110° , were treated with a rapid current of dry chlorine for one hour. On cooling, a mass of fine needles separated, consisting of 6-bromo-2-phenyl-1 : 3-benzoxazine-4-one, which, after washing with benzene, melted at 202° , and on recrystallisation from benzene at 207° . The yield was 5 grams, and the product was identical in all respects with that obtained by method 2 (see below): 0.4078, by Kjeldahl's method, required 13.7 c.c. *N*/10-HCl. *N* = 4.67. 0.4022 gave 0.2522 AgBr. Br = 26.68.

$C_{14}H_8O_2NBr$ requires *N* = 4.64; Br = 26.50 per cent.

2. Preparation from *O*-Benzoyl-5-bromosalicylamide.

The method employed was similar to that adopted by Titherley (Trans., 1910, **97**, 208), using anisole as a solvent. A very slow stream of dry hydrogen chloride was passed into a solution of 2 grams of *O*-benzoyl-5-bromosalicylamide (p. 28) in 10 c.c. of anisole at 150° contained in a small distilling flask. The anisole slowly distilled off, carrying with it the water formed in the reaction. The resulting yellow syrup, which solidified on cooling, was digested with 50 c.c. of dry boiling benzene. This left a quantity of *N*-benzoyl-5-bromosalicylamide (0.2 gram), and the filtrate, on cooling, deposited 6-bromo-2-phenyl-1 : 3-benzoxazine-4-one in a practically pure condition (1 gram), melting at 207° . On recrystallisation from benzene, it was obtained in small, white needles, melting at 208° :

0.1770, by Kjeldahl's method, required 6.0 c.c. *N*/10-HCl. *N* = 4.75. 0.1330 gave 0.0814 AgBr. Br = 26.04.

$C_{14}H_8O_2NBr$ requires *N* = 4.64; Br = 26.50 per cent.

The compound is sparingly soluble in cold alcohol, acetone, or benzene, but readily so in the hot solvents, and it is moderately soluble in cold chloroform. It is not acted on by cold dilute sodium hydroxide, but with strong aqueous or alcoholic ammonia it gives bright orange needles like the corresponding chloro-derivative. Dilute acids in the cold do not affect the bromo-derivative, but in hot alcoholic solution the ring undergoes disruption with addition of water, yielding *N*-benzoyl-5-bromosalicylamide (m. p. 240°), which separates as a voluminous mass, the yield being quantitative. This *N*-benzoyl derivative was identical with the product obtained by the rearrangement of *O*-benzoyl-5-bromosalicylamide (p. 28), and a

mixture of the two melted at 240° . It gave the following figures on analysis:

0.3648, by Kjeldahl's method, required 11.5 c.c. $N/10\text{-HCl}$. $N=4.41$.
0.1810 gave 0.1080 AgBr. $\text{Br}=25.53$.

$\text{C}_{14}\text{H}_{10}\text{O}_3\text{NBr}$ requires $N=4.38$; $\text{Br}=25.00$ per cent.

O-Benzoyl-5-bromosalicylamide, $\text{C}_6\text{H}_3\text{Br} \begin{matrix} \text{CO}\cdot\text{NH}_2 \\ \text{O}\cdot\text{COPh} \end{matrix}$.

A solution of 10 grams of 5-bromosalicylamide in 40 grams of pyridine (dried over barium oxide) was treated with 10 grams of benzoyl chloride with continued shaking. The temperature was kept at -15° during the addition, which occupied one and a-half hours, and the resulting bright red mixture was kept at -15° for a further hour. It was then treated with 50 c.c. of dry ether, the ethereal pyridine solution decanted off, and the yellow, solid mass treated with dilute sulphuric acid at 0° . An insoluble buff powder remained, consisting of the crude *O*-benzoyl derivative, which, after washing with water and ether, weighed 10 grams. On recrystallisation from boiling toluene, it separated in fine, colourless, glistening needles, melting at 154° :

0.6488, by Kjeldahl's method, required 20.3 c.c. $N/10\text{-HCl}$. $N=4.38$.
0.4528 gave 0.2620 AgBr. $\text{Br}=24.73$.

$\text{C}_{14}\text{H}_{10}\text{O}_3\text{NBr}$ requires $N=4.38$; $\text{Br}=25.00$ per cent.

O-Benzoyl-5-bromosalicylamide is sparingly soluble in the usual solvents. In boiling alcohol it dissolves, but almost immediately rearranges to the *N*-benzoyl isomeride (m. p. 238°), which separates on cooling slightly.

The same rearrangement occurs on melting, the liquid at 154° setting in about forty-five seconds to the solid *N*-benzoyl derivative, which then melts at 240° .

N-Benzoyl-5-bromosalicylamide, $\text{C}_6\text{H}_3\text{Br} \begin{matrix} \text{CO}\cdot\text{NH}\cdot\text{COPh} \\ \text{OH} \end{matrix}$.

Two grams of *O*-benzoyl-5-bromosalicylamide were dissolved in the least possible quantity of boiling alcohol, and the solution diluted to 200 c.c. with water at 80° . The temperature was then kept at the boiling point for a few minutes, when a thick, curdy precipitate of the pure *N*-benzoyl derivative, melting at 248° , was obtained. On recrystallisation from pure acetic acid, the melting point was raised to 249° :

0.4526, by Kjeldahl's method, required 14.2 c.c. $N/10\text{-HCl}$. $N=4.39$.
0.3142 gave 0.1842 AgBr. $\text{Br}=24.95$.

$\text{C}_{14}\text{H}_{10}\text{O}_3\text{NBr}$ requires $N=4.38$; $\text{Br}=25.00$ per cent.

N-Benzoyl-5-bromosalicylamide is very sparingly soluble in all the usual solvents, hot or cold. It may, however, be recrystallised from acetic acid if the operation be carried out fairly rapidly to avoid rearrangement. It gives intense yellow sodium and ammonium salts, which are sparingly soluble in water, from which, on acidification, the substance is precipitated in a colourless, gelatinous form.

Rearrangement.—One gram of the *N*-benzoyl derivative was boiled with 25 c.c. of glacial acetic acid for four hours. On cooling, 0.2 gram of unchanged substance separated out, and on diluting the filtrate with water, 0.5 gram of *O*-benzoyl-5-bromosalicylamide was obtained (m. p. 150°), which, on recrystallisation from toluene, melted at 154°. It was completely identical in all its properties with the synthetic product.

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IV.—*Synthesis of Camphoric Acid.*

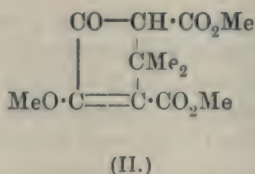
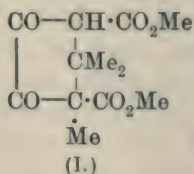
By GUSTAV KOMPPA.

A RECENT paper published simultaneously by G. L. Blanc and J. F. Thorpe in France (*Bull. Soc. chim.*, 1910, [iv], 7, 740) and England (*Trans.*, 1910, 97, 836), throwing doubt on my synthesis of camphoric acid, suggests that I could never have obtained that substance by the process described, and that my conclusions are based on an error. Although in a position to reply immediately to these critics, I thought it desirable first to make some complementary experiments, and at the same time possibly to show that Blanc and Thorpe are themselves mistaken in drawing somewhat hasty conclusions from their incomplete treatment of the subject. In this I have now succeeded, and the present communication is my reply to their arguments.

In the first place, the above-mentioned investigators declare that the basis of my synthesis, methyl diketoapocamphorate, cannot be produced in sufficient quantities (J. F. Thorpe, *Proc.*, 1909, 25, 94; G. L. Blanc, *Bull. Soc. chim.*, 1909, [iv], 5, xvi). Blanc even goes so far as to say in his address, "Le Camphre," delivered before the Société Chimique, "qu'il lui a été personnellement impossible de reproduire" this substance, and that the reaction according to which it was obtained "sur le papier ne présente pas grande chance de réussite." When I published a complete account of my researches, including the method of preparing the substance, they were able

to make use of the latter for their own experiments; they found it had the properties which I had previously described, although the yield which they obtained was not so good as it might have been according to my prescription. It is unnecessary to dispute this point, however, because it is not easy for a worker unfamiliar with this reaction to arrive at satisfactory results, towards the attainment of which I have been compelled to persevere for years. Nevertheless, my assistants, on becoming accustomed to the task, have usually been successful. For example, Mr. A. Lampén's yield varies from 45 to 70·5 per cent., Mr. B. Ingman's from 49 to 67 per cent., and Mr. W. Salvén's from 45 to 70 per cent., all being calculated as described in my paper. With the best intentions, it is not always possible to give a sufficiently detailed description of such a difficult and complicated method of preparation, and the yield may be affected by some condition as yet unknown; but I have had in my possession several hundred grams of methyl diketoapocamphorate.

The product obtained by Blanc and Thorpe on methylating this diketo-ester by my process was identical with mine, the melting point being 85—88°. In their last paper, these chemists argue that the methyl derivative is not, as I supposed, the *C*-methyl derivative (I), but the *O*-methyl ether (II):



This they claim to have proved by treating the methyl derivative melting at 85—88° with potassium hydroxide, obtaining an amount of potassium derivative corresponding with 50 per cent. of methyl diketoapocamphorate, and isolating from the mother liquor 40 per cent. of $\beta\beta$ -dimethylglutaric acid without detecting $\alpha\beta\beta$ -trimethylglutaric acid; according to this result, the methyl group in the diketo-ester melting at 85—88° is eliminated by alkali. On the supposition that the methyl group is not attached to carbon, they argue that I could not have obtained camphoric acid from the ester melting at 85—88°, and that my report is based on "an error." They have made this statement without having even tried to reduce the substance according to my directions. They do not even seek to explain what kind of error underlies my conclusions.

In considering whether a mistake has possibly been made, it is necessary to point out that if the methyl group were attached to oxygen instead of to carbon, reduction would lead to apocamphoric

acid as the final product. This melts at about the same temperature as *r*-camphoric acid, and although the appearance of the two substances under a microscope is not exactly similar, yet confusion is possible. But mixing together *apocamphoric* and *r*-camphoric acids causes a depression of 15—16° in the melting point, whereas the saturated acid which I obtained from the ester melting at 85—88° does not in the least depress the melting point of natural *r*-camphoric acid. Moreover, there is a difference of 45° in the melting points of the anhydrides of *apocamphoric* and camphoric acids. This fact, taken in conjunction with the dissimilar appearance, renders it impossible for any chemist to make such a mistake. Furthermore, I have not only synthesised *r*-camphoric acid and its anhydride, but also *r*-isocamphoric acid and *r*-dehydrocamphoric acid, which synthetical acids I have compared directly with the corresponding acids prepared from natural sources, demonstrating that these, when mixed together, do not effect a depression in the melting point, and that they are also in other respects identical. I attach a special significance to the identity of synthetic dehydrocamphoric acid with *r*-dehydrocamphoric acid prepared from *r*-camphoric acid. In 1903 I described the properties of dehydrocamphoric acid (*Ber.*, 1903, **36**, 4334), obtained synthetically from the ester melting at 85—88°, whilst only two years ago I procured this acid from natural *r*-camphoric acid, and showed that they were identical (*Annalen*, 1909, **370**, 212). That this synthetical dehydroacid cannot be the corresponding dehydro*apocamphoric* acid is clear also from the fact that the two acids, although having the same melting point, cause a depression of 14° when mixed together.

Even yet the facts are not all disclosed, but the foregoing is sufficient evidence that an earnest chemist could not possibly commit an error such as Blanc and Thorpe would suggest, and that the experimental results, as I have stated them to be, can be established.

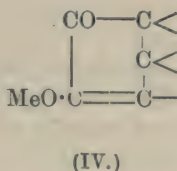
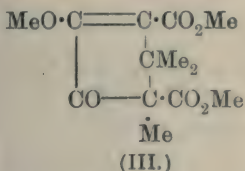
In his quoted paper, Thorpe lays special stress on the passage: "It was from the pure crystalline material that Komppa prepared camphoric acid." As it appears from my laboratory notes that the methyl diketocamphorate used for my synthesis had been crystallised once only, I deemed it important to show that the camphoric acid I obtained could not have arisen from any possible impurities in the diketo-ester. Accordingly, with the assistance of Dr. O. Routala, I have again prepared a thoroughly purified ester melting at 85—88°, and reduced it, first with sodium amalgam and then with hydrogen iodide, precisely as was stated in my complete report (*Annalen*, 1909, **370**, 209), obtaining once more the same yield of the same dehydro-acid, melting at 223—224° (normal thermometer);

the product, when mixed with *r*-dehydrocamphoric acid, again failed to cause depression of the melting point. This is the fifth occasion on which, with the aid of three different assistants, I have completely synthesised the acid; as it is identical with *r*-dehydrocamphoric acid prepared from *r*-camphor, and as I have also three times, with two different assistants, changed this synthetical dehydroacid into *r*-camphoric acid and also into *isocamphoric acid*, it seems to me wholly impossible that other chemists should fail to prepare camphoric acid from the same substance.

But how is it to be explained that Blanc and Thorpe have not even tried to reduce the substance melting at 85—88°, in order to ascertain whether they could obtain camphoric acid or dehydrocamphoric acid according to my method? It is evident from the discussion following Thorpe's paper that the reason for this neglect was the supposition that, because the methyl group is removed by alkali from the ester melting at 85—88°, it is also removed by reducing, according to my prescription, with sodium amalgam followed by hydriodic acid. Here they have made the serious mistake of not taking into account the fact that I do not reduce in caustic alkali solution, but in alkali carbonate, or rather in alkali bicarbonate, a rapid stream of carbon dioxide being led, during the whole operation, through the reducing solution. That sodium carbonate does not eliminate the methyl group from the substance melting at 85—88° must be known to them, because in preparing the latter according to my method they separated it from the neutral product of methylation by extracting it several times with sodium carbonate solution, and isolating the ester by acidifying this liquid. It would surely have been worth while to reduce the ester in question by my process, even if the methyl group is eliminated by caustic alkali, a point which I have not yet had time to verify.

I do not, however, admit that the ester melting at 85—88° is the *O*-methyl derivative (II), as claimed by Blanc and Thorpe on account of its behaviour towards alkali, because camphoric and dehydrocamphoric acids can be synthesised from it. That this ester is, as I have supposed from the outset, the *C*-methyl derivative is demonstrated in the following manner. The ester in question produces, in common with all α -diketones, a yellowish-brown colouring matter (quinoxaline), which has a strong green fluorescence when dissolved in ether and in alcohol, developing with mineral acids a dark red coloration destroyed by water, properties which characterise quinoxalines. I have not succeeded in crystallising this colouring matter, or the one from *o*-tolylenediamine, and have therefore not been able to analyse it. When one takes into account the fact that the neutral ether, obtained by methylating diketo-

apocamphoric ester, and to which I have ascribed the following constitution (III):



does not give the above-mentioned fluorescence, although it contains the same grouping of elements (IV) which Blanc and Thorpe suppose to exist in the ester melting at 85—88°, the coloration observed is not to be ignored. The difference in constitution between the ester melting at 85—88° and the neutral ester (III) is indicated more plainly when phenylenediamine hydrochloride is used instead of the free base. With this agent, the ester melting at 85—88° develops a red coloration at the ordinary temperature, and slight heating produces the effect very easily, this intense red solution not being given by the neutral ester (III). Attempts to produce osazones from the ester melting at 85—88° have led to oils, which have not been investigated further.

The constitutional formulæ which I have ascribed to these substances are confirmed by the following determinations of the methoxy-group according to Zeisel's method:

0.2500 (ester m. p. 85—88°) gave 0.4495 AgI. MeO = 23.74.

0.2000 " " " 0.3620 AgI. MeO = 23.89.

Formula I requires 24.22; formula II requires 36.33 per cent.

0.2106 (neutral ether) gave 0.5223 AgI. MeO = 32.76.

Formula III requires 34.44 per cent.

As the methyl group in the ester melting at 85—88° is not removed by boiling hydriodic acid, it is certainly not attached to oxygen, as suggested by Blanc and Thorpe, thus indicating the constitution (formula I) which I have already advocated, namely, that of diketocamphoric ester.

From all these facts, it is evident that the criticisms of my camphoric acid synthesis put forward by Blanc and Thorpe are completely baseless.

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V.—*Hydroxycodine: a New Alkaloid from Opium.*

By JAMES JOHNSTON DOBBIE and ALEXANDER LAUDER.

THE new opium alkaloid, which forms the subject of this communication, was discovered by Messrs. T. and H. Smith, of Edinburgh, who were good enough to place a small quantity of the hydrobromide in our hands for investigation. The alkaloid is found in very small quantity in the last mother liquors obtained in the working up of the opium alkaloids, after all the other alkaloids have been eliminated.

The alkaloid is readily soluble in water, alcohol, ether, chloroform, benzene, or amyl alcohol, but, so far, has not been obtained in a crystalline condition. From all these solvents it separates in the form of a varnish. The alkaloid has no definite melting point; on heating, it begins to soften about 40°, and is completely melted at 51°.

Of the common salts, the *hydrobromide* and the *hydrochloride* both crystallise well; the hydrobromide is, however, much less soluble than the hydrochloride, and it was therefore selected for analysis. It readily crystallises from water in large, hard, prismatic crystals, which contain no water of crystallisation. The crystals were dried at 100°, and gave the following results on analysis:

0.3344 gave 0.6678 CO₂ and 0.1808 H₂O. C=54.46; H=6.00.

0.3318 „ 0.6614 CO₂ „ 0.1680 H₂O. C=54.36; H=5.62.

0.4502 „ 14 c.c. N₂ (moist) at 17° and 742 mm. N=3.52.

0.2988 „ 9 c.c. N₂ (moist) „ 14.4° and 754 mm. N=3.50.

0.6056 „ 0.284 AgBr. Br=19.95.

0.5210 „ 0.244 AgBr. Br=19.92.

Mean, C=54.41; H=5.81; N=3.51; Br=19.94.

C₁₈H₂₁O₄N.HBr requires 54.54; H=5.55; N=3.53;

Br=20.20 per cent.

Platinichloride.—The alkaloid was dissolved in dilute hydrochloric acid, and precipitated with excess of platinum chloride; the precipitate was well washed, and dried at 100° for analysis:

0.3258 gave 0.4942 CO₂ and 0.1296 H₂O. C=41.36; H=4.42.

0.2452 „ 0.3725 CO₂ „ 0.0975 H₂O. C=41.43; H=4.44.

0.2744 „ 7 c.c. N₂ (moist) at 14° and 755 mm. N=2.98.

0.1768 „ 0.0328 Pt. Pt=18.55.

0.2764 „ 0.2280 AgCl. Cl=20.39.

(C₁₈H₂₁O₄N)₂H₂PtCl₆ requires C=41.54; H=4.23; N=2.69;

Pt=18.75; Cl=20.48 per cent.

Determination of Methoxyl Groups.—The number of methoxy-groups was determined by Zeisel's method:

0.4052 gave 0.2408 AgI. OMe=7.82.

0.3426 „ 0.2064 AgI. OMe=7.93.

OMe·C₁₇H₁₈O₃N·HBr requires OMe=7.83 per cent.

Methiodide.—The methiodide was prepared by dissolving a small quantity of the alkaloid in a mixture of methyl iodide and methyl alcohol. The methiodide separated in colourless plates. It was recrystallised from methyl alcohol, and dried over sulphuric acid:

0.2076 gave 0.1098 AgI. I=28.57.

C₁₉H₂₄O₄NI requires I=27.79 per cent.

This result is sufficient to show that the alkaloid is a tertiary base.

Specific Rotation.—An aqueous solution of the hydrobromide is slightly dextrorotatory:

I. 5.1884, in 100 of water, gave, in a 1-dcm. tube at 20°, $\alpha + 0.9^\circ$; D_4^{20} 1.0158; whence $[\alpha]_D^{20} + 17.07^\circ$.

II. 5.0741, in 100 of water, gave, in a 1-dcm. tube at 20°, $\alpha + 0.9^\circ$; D_4^{20} 1.0154; whence $[\alpha]_D^{20} + 17.4^\circ$.

Colour Reactions.—With Fröhde's reagent, the new alkaloid gives a yellowish-green colour, which gradually changes to blue; and with Mandelin's reagent a yellowish-green, also changing to blue on keeping. These reactions are practically identical with those given by codeine with the same reagents.

Absorption Spectra.—The absorption spectra of an aqueous solution of the hydrobromide were photographed. The spectra show a well-marked absorption band at $1/\lambda$ 3500. The position of this band is identical with that of codeine (Hartley, *Phil. Trans.*, 1885, Part II, 471; Dobbie and Lauder, *Trans.*, 1903, **83**, 605), but the codeine band is very slightly more persistent.

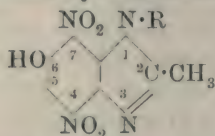
The discoverers propose the name *neopine* for the new alkaloid. Although, owing to the small quantity of material at our disposal, the chemical evidence is still incomplete, the alkaloid is almost certainly a hydroxycodine, but it is not identical with the hydroxycodine prepared by Ach and Knorr (*Ber.*, 1903, **36**, 3067) by the oxidation of codeine. Its formula differs from that of codeine only in the possession of an additional atom of oxygen, which, owing to the solubility, is probably present in an hydroxyl group. Like codeine, it contains only one methoxyl group. Further evidence of the close relation between the two alkaloids is afforded by the practical identity of their absorption spectra.

The physiological action of the new alkaloid has been investigated by Professor Stockman, of Glasgow University.

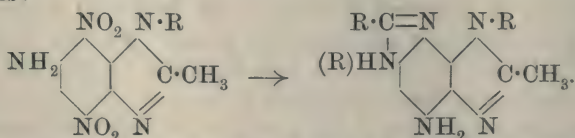
VI.—*Syntheses with Phenol Derivatives Containing a Mobile Nitro-group. Part III. Complex Iminazoles, Azo-compounds, and Azides.*

By RAPHAEL MELDOLA and HAROLD KUNTZEN.

THE extreme mobility of the 3-nitro-group in 2:3:5-trinitro-4-acetylaminophenol when the latter compound is allowed to interact with primary amines has been taken advantage of for the synthesis of iminazoles and other compounds and for the study of the influence of the position of substituents in determining the yield of iminazole, etc. (Trans., 1906, **89**, 1935; 1908, **93**, 1659; 1909, **95**, 1033). The object of the present extension of the research was, in the first place, to ascertain whether complex iminazoles containing two iminazole rings attached to one benzene nucleus were capable of existence. Although the results in this direction have not hitherto been promising, we think it desirable to place upon record the principle which has been adopted, because we propose continuing the experiments in this direction. It will be seen from the general formula of the iminazoles synthesised by this method:



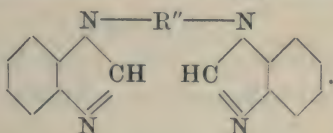
that there are two groups in the benzene ring which might, under suitable treatment, be made to furnish the iminazole ring, namely, the 6-hydroxy- and 7-nitro-group. If, by the action of ammonia or amines on the iminazoles or their ethers (Trans., 1908, **93**, 1672, etc.), an amino-group or substituted amino-group could be substituted for the 6-hydroxyl group, dinitro-derivatives would be formed, which, on acylation and reduction, might be expected to furnish compounds of the type of the hitherto unknown benzdi-iminazoles:



Many experiments have been made with the methyl ether of the iminazole from aniline and the trinitro-compound, but the difficulty appears to be the initial step of substituting the amine residue for the 6-hydroxy-group. It is well known, however, that the mobility

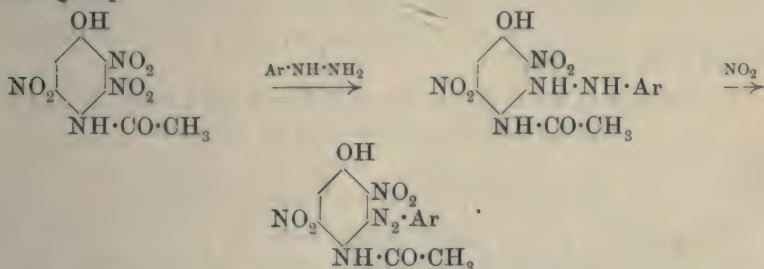
of the alkyloxy-group increases with the weight of the radicle attached to the oxygen atom, and the experiments will be continued with ethers containing the higher homologues of methyl.

The other direction in which the research has been pursued had also for its object the synthesis of compounds containing two iminazole rings, but linked by a bivalent radicle. Compounds of this type would differ from the foregoing benzdi-iminazoles, and might be termed bisiminazoles. The type would be:



As will be seen from the experimental section of this paper, a compound of this type has been prepared, but owing to its colloidal character and the difficulty of obtaining any definite crystalline derivatives, it has not been found possible to characterise the pure substance.

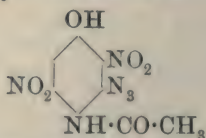
The formation of azo-derivatives by the interaction of the trinitro-compound and hydrazines was indicated in a former paper (Trans., 1906, 89, 1943). This new synthesis of azo-compounds by direct substitution in the benzene nucleus has been further studied, and the conditions which favour the maximum yield have been experimentally ascertained. In this reaction, an intermediate hydrazo-compound is formed by catenation, and from the latter the azo-compound is formed by the oxidising action of the eliminated nitro-group:



In connexion with this synthesis, it has been discovered that secondary hydrazines of the types: $\text{Ar}_2\text{N}\cdot\text{NH}_2$, $\text{ArRN}\cdot\text{NH}_2$ do not form azo-compounds, whereas all primary hydrazines readily undergo condensation with the trinitro-compound. Thus, phenyl-, tolyl-, and nitrophenyl-azo-compounds are readily obtained from the trinitro-compound and the respective hydrazines, whilst phenylmethylhydrazine and diphenylhydrazine give only resinous products, arising partly from the breaking down of the trinitro-compound, and

partly from the decomposition of the hydrazine by the eliminated nitro-group.

Another synthesis made possible through the mobility of the 3-nitro-group is that of azides (triazo-compounds), the trinitro-compound reacting readily with sodium azide to form the compound :



2 : 5-Dinitro-4-acetyl-amino-3-triazophenol.

The other product of the reaction is sodium nitrite.

EXPERIMENTAL.

The Iminazole from the Trinitro-compound and Acetyl-p-phenylenediamine.

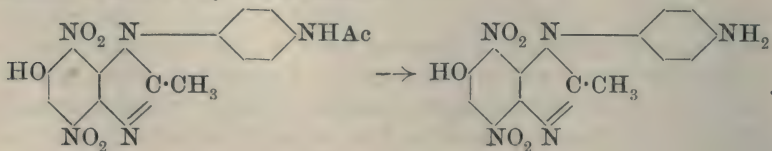
As the trinitro-compound does not give the aminoiminazole required as an intermediate product by interaction with *p*-phenylenediamine (Trans., 1909, **95**, 1033), the acetyl derivative of the latter was made use of. The trinitro-compound and three molecular proportions of acetyl-*p*-phenylenediamine were boiled together in alcoholic solution for two hours, the product was extracted by dilute hydrochloric acid, and purified by alternate alkaline and acid treatment in the way described in connexion with all the other iminazoles synthesised by our method. Two grams of trinitro-compound gave 2.13 grams of iminazole. 4:7-Dinitro-6-hydroxy-1-*p*-acetylaminophenyl-2-methylbenziminazole crystallises from alcohol, in which it is very sparingly soluble, in dense, ochreous scales, melting at 261.5°:

0.0722 gave 11.9 c.c. N₂ (moist) at 15° and 742.4 mm. N=18.85.

C₁₆H₁₃O₆N₅ requires N=18.87 per cent.

Hydrolysis of the Acetylaminiminazole.

The removal of the acetyl group and the purification of the resulting aminoiminazole has proved a task of the greatest difficulty, and numerous unsuccessful experiments were carried out before the required compound was obtained. The synthesis which had to be realised is shown by the formulæ:



Alkaline hydrolysts are ineffective, and after many trials it was found that strong sulphuric acid was the best hydrolysing agent for the purpose. The acetyl derivative is not basic, but dissolves in cold concentrated sulphuric acid, and is precipitated on dilution with water. In order to effect the hydrolysis, the acetyl derivative is dissolved in concentrated sulphuric acid, a little water added (not enough to precipitate the substance), and the solution heated until a drop remains clear on dilution with water, thereby showing that the basic aminoiminazole has been formed. If the sulphuric acid is too strong or the temperature raised above the point at which hydrolysis is shown to have taken place by the test described, complete decomposition ensues, and the materials are lost. After hydrolysis, the solution is diluted with water, filtered, if necessary, and exactly neutralised with ammonia. The precipitate is collected, washed, and purified by solution in dilute hydrochloric acid, filtering, and reprecipitating with ammonia. This treatment is necessary, because some of the acetyl derivative escapes hydrolysis, and on dilution and neutralisation the precipitate appears to contain, not only the required basic amino-compound, but also a salt of the latter with the unchanged acid acetyl derivative. It is unsafe to carry the hydrolysis to the extreme point on account of the tendency to undergo decomposition.

The purification of the aminoiminazole after separation from the unchanged acetyl derivative presented great difficulties on account of the combined phenolic and basic character of the molecule. The compound forms salts with both acids and bases, so that some difficulty was experienced in preparing a pure specimen for analysis. After many trials, it was found that the compound formed an ammonium salt, which crystallised from water in stumpy, dull orange needles:

0.0756 gave 15.6 c.c. N_2 (moist) at 16° and 768 mm. $N = 23.99$.

$C_{14}H_{14}O_5N_6$ requires $N = 24.28$ per cent.

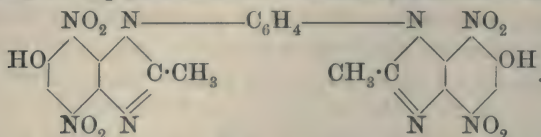
This ammonium salt, when dissolved in water and decomposed by exact neutralisation with dilute hydrochloric acid, gives the free 4:7-dinitro-6-hydroxy-1-p-aminophenyl-2-methylbenziminazole as an ochreous, microcrystalline powder, very sparingly soluble in boiling alcohol, and separating from the latter solvent in ochreous nodules, having no definite melting point, but decomposing with charring from about 215° :

0.1800 gave 32.5 c.c. N_2 (moist) at 18.5° and 756.5 mm. $N = 20.7$.

$C_{14}H_{11}O_5N_5$ requires $N = 21.21$ per cent.

On account of the difficulty of crystallising the substance, no further purification was attempted, but the product was acted on by trinitro-compound, as described below,

Synthesis of the Bisiminazole: 4:4':7:7'-Tetranitro-6:6'-dihydroxy-1:1'-p-phenylene-2:2'-dimethylbisbenziminazole.



The aminoiminazole obtained as above was boiled in alcoholic solution with trinitro-compound in the proportion of one molecule of the latter to two of the former, and the ochreous granular substance, which separated in the course of two or three hours, was submitted to the acid and alkaline treatment generally adopted. There is no doubt that the product is the bisiminazole required, but it was found impossible to crystallise it from any solvent, and no specimen pure enough for analysis could be obtained. The compound is extremely insoluble in all the usual organic solvents, and the minute quantity which does dissolve separates out in a colloidal state on cooling. It is phenolic in character, dissolving in dilute alkalis with an orange colour, and being precipitated by acids as a brown, gelatinous mass, which dries to a brittle, brown resin. On adding silver nitrate to a solution of the ammonium salt, a brown, gelatinous, insoluble *silver* salt is precipitated, and this also dries to a brown resin. Analyses of this resin gave:

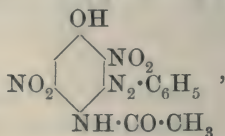
Found, Ag=27.74 and 29.43.

$C_{22}H_{12}O_{10}N_8Ag_2$ requires Ag=28.26 per cent.

The general properties of this new type of substituted bisiminazoles are not such as to encourage a further detailed study of the compound. The existence of the type having, however, been established, we propose extending the research with a view to preparing the isomeride containing the *m*-phenylene nucleus, in the hope that this compound may be more amenable to treatment by ordinary chemical methods.

Synthesis of Azo-compounds.

3-Benzeneazo-2:5-dinitro-4-acetylaminophenol,



has already been described (Trans., 1906, **89**, 1943) in a preliminary way, and a further study of the compound now enables us to give more complete and more correct details concerning its mode of

formation and properties. In the first place, we have found that in order to ensure the production of a pure compound, the trinitro-acetylaminophenol and phenylhydrazine must be allowed to interact only in equimolecular proportions. If excess of phenylhydrazine is present, some secondary reaction with the azo-compound takes place, and products arising from the reduction of the latter are formed. These impurities are extremely difficult to remove, and their association with the azo-compound tends to disguise the characters of the latter. Our first preparation of decomposing point 188° was no doubt contaminated to a sufficient extent to depress the decomposing point, as we now find that the pure compound decomposes at 248° .

In order to prepare the azo-compound, equimolecular proportions of the trinitro-compound and of phenylhydrazine are dissolved in a small quantity of alcohol, and the solution is warmed until the red crystalline salt, which at first separates out, passes into solution. When this stage has been reached it is better to remove the flask from the water-bath and to allow the reaction to complete itself at the ordinary temperature. In the course of twelve hours, the formation of the azo-compound is complete, and the crystalline deposit can be collected, washed with alcohol, and crystallised from boiling glacial acetic acid. From this solvent it separates in large, ruby-red prisms, with a slight metallic lustre. It is but very sparingly soluble in boiling alcohol, but dissolves more readily in boiling pentachlorethane, forming a red solution, from which scarlet needles separate on cooling. The specimen used for analysis was crystallised from glacial acetic acid:

0.1318 gave 0.2350 CO_2 and 0.040 H_2O . $\text{C}=48.62$; $\text{H}=3.37$.

0.0783 „ 13.8 c.c. N_2 (moist) at 17° and 761.5 mm. $\text{N}=20.64$.

$\text{C}_{14}\text{H}_{11}\text{O}_6\text{N}_5$ requires $\text{C}=48.68$; $\text{H}=3.21$; $\text{N}=20.29$ per cent.

The azo-compound dissolves in concentrated sulphuric acid with an orange colour, and is precipitated unchanged on dilution with water. Attempts to eliminate the acetyl group by acid and alkaline hydrolysts led to negative results, the compound either not being hydrolysed or else decomposing completely. The hydroxyl group confers phenolic characters on the compound, and it forms alkaline salts, which are completely insoluble in presence of the slightest excess of alkali. The *sodium* salt is of a deep violet colour, insoluble in cold water, and dissolving in hot water with a dull red colour. On the addition of acid, the azo-compound is precipitated from the hot aqueous solution of the sodium salt in the colloidal state.

The azo-compound can be acetylated by keeping it in acetic anhydride solution in the presence of a small quantity of concentrated sulphuric acid for several days. Specimens withdrawn

from time to time and analysed showed that the substitution of acetyl for the hydroxylic hydrogen takes place but slowly. The product, which is precipitated as a dark, ochreous, crystalline powder on diluting the solution with water, melts and decomposes at about 203° :

0.0671 gave 10.5 c.c. N_2 (moist) at 15.5° and 761.3 mm. $N = 18.31$.

$C_{16}H_{13}O_7N_5$ requires $N = 18.09$ per cent.

This *acetyl* derivative decomposes on boiling with glacial acetic acid, with the evolution of nitrous fumes and the formation of some insoluble resinous product, together with a definite compound which crystallises out from the solution, on cooling, in ochreous needles. The latter, by repeated crystallisation from glacial acetic acid, were finally obtained with a definite decomposing point of $284-285^{\circ}$, and containing nearly the same percentage of nitrogen (18.2 and 18.01) as the original acetyl derivative, but less carbon. This product of decomposition appears to be of interest, but we have not yet been able to determine its constitution, and its study will be resumed.

3-*p*-Nitrobenzeneazo-2:5-dinitro-4-acetylaminophenol.

In order to prepare this compound, *p*-nitrophenylhydrazine and trinitroacetylaminophenol are dissolved in a small quantity of alcohol, the hydrazine being in slight excess of the quantity calculated for one molecular proportion of each compound. The solution is kept warm on the water-bath for an hour, care being taken to prevent actual boiling. On removing from the source of heat, and allowing to remain for some hours, the azo-compound separates out in crystalline nodules, which can be purified by washing with alcohol containing hydrochloric acid and crystallisation from glacial acetic acid. The compound dissolves in this last solvent with a deep orange colour, and separates, on cooling, in dark brown, glistening prisms, which appear ruby-red by transmitted light. It melts and decomposes at $244-245^{\circ}$:

0.1308 gave 23.8 c.c. N_2 (moist) at 13.5° and 765.5 mm. $N = 21.61$.

$C_{14}H_{10}O_8N_6$ requires $N = 21.55$ per cent.

This azo-compound can also be acetylated by prolonged action of acetic anhydride in presence of a little concentrated sulphuric acid. After five days at the ordinary temperature, a *diacetyl* derivative is formed, which consists of an ochreous, crystalline powder, decomposing at $160-168^{\circ}$:

0.0744 gave 12.65 c.c. N_2 (moist) at 17° and 761.4 mm. $N = 19.76$.

$C_{16}H_{12}O_9N_6$ requires $N = 19.45$ per cent.

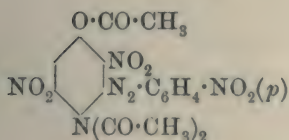
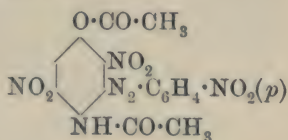
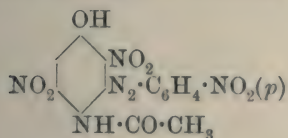
At the end of nine days under the same conditions, another acetyl

group is introduced, the resulting *triacetyl* derivative consisting of an ochreous, micro-crystalline powder, decomposing at 162—164°:

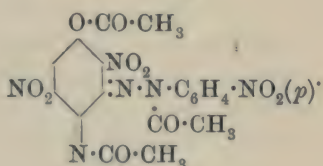
0.1926 gave 29.6 c.c. N_2 (moist) at 19.5° and 767.7 mm. $N = 17.57$.

$C_{18}H_{14}O_{10}N_6$ requires $N = 17.73$ per cent.

These acetyl derivatives are decomposed on boiling with glacial acetic acid, with the evolution of nitrous fumes and the formation of resinous products. As all the compounds described under this section are new, the formulæ are subjoined:



or



2: 5-Dinitro-4-acetylamino-3-triazophenol.

The trinitro-compound readily exchanges the 3-nitro-group for the triazo-group by interaction with sodium azide. A slightly warm aqueous solution of the latter is prepared, and to this the solid trinitro-compound is added in small portions. After some hours at the ordinary temperature, a crystalline deposit forms, and a further quantity of the triazo-compound is precipitated from the solution on acidifying with hydrochloric acid. The product, after being collected and washed with water, crystallises from alcohol in flat, ochreous needles or golden scales, melting at 167—168°:

0.1288 gave 32.5 c.c. N_2 (moist) at 15.3° and 765.9 mm. $N = 29.73$.

$C_8H_6O_6N_6$ requires $N = 29.81$ per cent.

The compound is phenolic in character, dissolving in alkalis with an orange colour and being reprecipitated by acids.

The triazo-compound could not be methylated either by methyl sulphate and alkali, or by silver oxide and methyl iodide. Attempts to remove the acetyl group by acid and alkaline hydrolysts led to negative results, the compound resisting hydrolysis or decomposing completely. Acetylation was effected in the usual way by means of acetic anhydride and sulphuric acid. After three days a product was obtained which, from the results of analysis, appeared to be a mixture of a *diacetyl* and a *triacetyl* derivative, and from

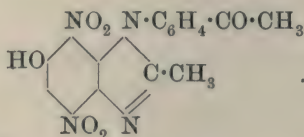
which, by repeated crystallisation from alcohol, the former was isolated in nodular tufts of yellow needles, melting at $140-141^{\circ}$:

0.0420 gave 9.3 c.c. N_2 (moist) at 17° and 759.2 mm. $N=25.66$.

$C_{10}H_8O_7N_6$ requires $N=25.90$ per cent.

On contact with dilute alkali the *O*-acetyl group is at once eliminated, and the original triazo-compound regenerated.

The Iminazole from the Trinitro-compound and Aminoacetophenone: 4:7-Dinitro-6-hydroxy-1-p-acetylphenyl-2-methylbenz-iminazole.



This compound was prepared in the usual way by boiling an alcoholic solution containing the trinitro-compound and two molecular proportions of aminoacetophenone for about an hour, when the iminazole separates out in ochreous scales. Purification could not be effected in this case by the usual method of alkaline treatment, as the compound is resinified by the action of alkalis. After crystallisation from alcohol, in which it is but sparingly soluble, the compound consists of ochreous scales, melting somewhat vaguely with decomposition at 246° :

0.0624 gave 8.2 c.c. N_2 (moist) at 16.5° and 768 mm. $N=15.55$.

$C_{16}H_{12}O_6N_4$ requires $N=15.74$ per cent.

By the action of hydroxylamine acetate an *oxime* was obtained, which crystallised from alcohol in small, ochreous scales, melting at 223° :

0.0630 gave 10.3 c.c. N_2 (moist) at 13° at 754 mm. $N=19.16$.

$C_{16}H_{13}O_6N_5$ requires $N=18.88$ per cent.

The iminazole reacts also with phenylhydrazine, forming a *phenylhydrazone*, which crystallises from alcohol in ochreous nodules having a vague decomposing point of about 198° .

During much of this work we had the co-operation of Mr. J. Gordon Hay, to whom we desire to express our thanks.

FINSBURY TECHNICAL COLLEGE.

VII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part I. The Rotations of the Simplest Secondary Alcohols of the Fatty Series.*

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

THE authors hope to communicate to the Society a series of papers in which will be discussed the qualitative and quantitative dependence of rotatory power on chemical constitution, and feel it desirable to state at the outset their reasons for commencing yet a further investigation of this interesting problem.

It is obvious that in the present state of knowledge much of the previous work * in this field is very difficult to correlate even in a qualitative manner. Now there are numerous investigations of the type, as, for example, (a) the very extended and careful researches of P. F. Frankland and his co-workers on the rotatory powers of derivatives of the optically active glyceric and tartaric acids; (b) the independent work of Tschugaeff and of Rupe on the bornyl and menthyl esters of various acids, and (c) the paper of one of us and Littlebury on the esters of *l*-menthylcarbamic acid, in which in each case the effect of various substituents on the rotatory power of some one optically active substance has been studied; that is to say, in the above instances the effect of substituting the alcoholic or carboxylic hydrogen atoms in glyceric and tartaric acids, in borneol, menthol, and menthylcarbamic acid. In the compounds described in such investigations the substituent is not attached to an asymmetric carbon atom, and is in many cases far removed from it in the molecule, whilst in several of the parent substances of such investigations there are more than one such carbon atom. It is thus often impossible to decide how far the effect of the substituent is due to its relative mass and how far to its structure, this particularly being the case in compounds containing the menthyl radicle (compare Pickard and Littlebury, *Trans.*, 1907, **91**, 301).

In addition to this difficulty there is also the additional one that it is often doubtful whether conclusions drawn from one group of comparatively complex compounds can be applied safely to those drawn from another group of widely differing constitution. Thus, for example, confusion may be introduced if the effect on the rotatory power of substituting the alcoholic hydrogen atoms be compared in such widely different compounds, as, for example, glyceric acid, menthol, or the

* Up to the end of 1904 this is admirably summarised by Walden (*Ber.*, 1905, **38**, 345).

optically active amyl alcohol of fusel oil. Again, many of the compounds compared in such investigations are solids at the ordinary temperature, and the rotations of these have been determined in solution, although the effect of solvents on rotatory power is as yet little understood. Further, the effect of temperature on the rotatory powers of the pure liquids, considerable as it is in many cases, has been often disregarded, although in this respect the investigations of Frankland leave little to be desired.

These and similar difficulties are well exemplified when a comparison is made of the rotatory powers of the various compounds of β -phenylpropionic, cinnamic, and phenylpropionic acids which have been prepared by several investigators to show the relative effect of unsaturation on optical activity.

In table I will be found a list of the molecular rotatory powers of several of the compounds previously described, and also those of the esters of the three acids with *d*- and *l*-methyl-*n*-hexylcarbinol (Trans., 1907, 91, 2058). These esters of a simple secondary alcohol give results differing from those obtained with more complicated secondary alcohols, such as menthol and borneol.

TABLE I.

Molecular Rotatory Powers of Esters and Salts of β -Phenylpropionic, Cinnamic, and Phenylpropionic Acids.

Ester or Alkaloid.	Acid.		
	β -Phenylpropionic.	Cinnamic.	Phenylpropionic.
<i>l</i> -Amyl alcohol *	+5.0°	+16.4°	+12.1°
(Methylethylcarbinol)			
<i>l</i> -Menthol †	-161.9	-247.8	—
„ ‡	178.3	235.5	-215.9
„ § { <i>a</i>	171.5	171.6	-166.7
„ § { <i>b</i>	162.6	184.3	157.6
<i>d</i> -Borneol § { <i>a</i>	+86.5	+82.5	+87.6
„ § { <i>b</i>	82.9	82.6	89.4
<i>d</i> -Methyl- <i>n</i> -hexylcarbinol 	+32.1	+104.4	+131.1
<i>l</i> -Methyl- <i>n</i> -hexylcarbinol 	-32.8	-103.4	-130.9
Coniine ¶	-5.1	-20.6	-19.7
Cinchonine ¶	+381.9	+475.2	+511.6

* Walden (*Zeitsch. physikal. Chem.*, 1896, 20, 569). In the nomenclature of Marckwald (*Ber.*, 1902, 35, 1599), this alcohol is *d*-amyl alcohol.

† Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 606).

‡ Rupe (*Annalen*, 1909, 369, 311). Determinations in 10 per cent. benzene solution.

§ Hilditch (Trans., 1908, 93, 14). Determinations in 10 per cent. solution, (*a*) in chloroform, (*b*) in acetone.

|| The unsaturated esters have been quantitatively reduced to the saturated ester (see page 67).

¶ Hilditch (Trans., 1908, 93, 713). Determinations in 4 per cent. chloroform solution.

These results (table I) show at once that no general conclusions can be drawn as to the quantitative effect on the rotatory powers of the alcohols and alkaloids named when the alcoholic hydrogen atom is displaced by acid radicles (or salts are formed with acids) of closely related constitution, but differing in the degree of unsaturation, for in some cases the ethylenic, and in the others the acetylenic, compound has the greater rotation.

It is, however, convenient at this juncture to recall that the vast amount of painstaking and laborious work in this field has led to certain well-founded, but very wide, generalisations. These need not now be re-stated, but are well exemplified by the investigations quoted in the table, which (with others) show that (we believe in every known case) the effect of unsaturation is exhibited in the exaltation of rotatory power.

Considerations such as these make the following conditions desirable for a re-investigation of this subject: (1) the active compounds compared should contain only one asymmetric carbon atom; (2) the effect of various radicles on the rotatory power should only be compared when these are attached directly to the asymmetric carbon atom, and (3) the compounds should be liquids and their rotatory powers should be measured in the pure state and at different temperatures.

Thus, whilst previous investigators have as a rule studied the variation in the rotatory power of some one compound caused by inactive substituents, the object of the present authors is to compare the rotatory powers of different series of comparatively simple compounds. Optically active compounds, however, of the type required are very little known, and it becomes therefore necessary to prepare them specially.

No class of compounds seems so likely as the alcohols to fulfil in general the third condition laid down, whilst the ease with which all types of alcohols can now be synthesised, thanks to the Grignard reaction and the catalytic reactions of the Toulouse school, makes this class of compounds particularly suitable for the purpose in view. Now one of us and Littlebury have described (Trans., 1907, 91, 1973) a method for what is believed to be the complete resolution of racemic alcohols, namely, by the fractional crystallisation of the salts formed by the combination of various optically active bases with the acid esters of the alcohol and a polybasic acid, whilst the present authors in a similar way carried out the first successful resolution (*loc. cit.*) of an aliphatic alcohol, namely, that of methyl-*n*-hexylcarbinol with $[\alpha]_D^{17} \pm 9.9^\circ$. The method has since been found to be a general one, and can be applied to several types of alcohols (see preliminary note, Proc., 1909, 25, 167); therefore, those types of alcohols which contain one asymmetric carbon atom, since they can be synthesised

and resolved into their optically active components, and since they have as a rule low melting points, appear to be very suitable for a re-investigation of the problem of the dependence of rotatory power on chemical constitution.

However, before describing the results obtained so far in this direction, attention should be called to the following evidence, which will furnish an answer to the very obvious question as to whether such results might not be vitiated by an incomplete resolution of the racemic alcohols. Now, firstly, that the method has effected complete resolutions in some cases seem certain. For example, one of us and Littlebury (*loc. cit.*) prepared by this method four borneols, which all severally gave, when oxidised, camphors identical in rotatory power with the maximum exhibited by the natural products; thus the *d*-borneol and the *l*-isoborneol prepared each gave pure *d*-camphor, whilst the *l*-borneol and the *d*-isoborneol gave pure *l*-camphor. Again, the *d*-methyl-*n*-heptylcarbinol described below has an equal but opposite rotatory power to that of the specimen of the same compound isolated from oil of rue by Power and Lees* (*Trans.*, 1902, 81, 1592). Secondly, in the case of the fourteen alcohols, the resolutions of which are described below (with two exceptions),† there have been obtained either both the dextro- and lævo-rotatory forms of the alcohols with equal and opposite rotations, or both forms of the same acid ester with equal and opposite rotation, or two preparations of the same acid ester having identical rotations by fractional crystallisation of the salts of two different alkaloids or two preparations of the alcohol with identical positive rotation from two different acid esters. Thirdly, the recorded rotatory powers (see table II, p. 49) of the alcohols belonging to the same series show a gradual alteration as the series is ascended, and thus agree well one with the others. Fourthly, an exhaustive series of experiments failed to give any evidence against the optical purity of methyl-*n*-hexylcarbinol with $[\alpha]_D^{17} \pm 9.9^\circ$. In these, (a) the diethyl and dimethyl esters of *d*- and *l*-tartaric acid were allowed to remain in presence of hydrogen chloride with an excess or a deficiency of the *d*- or the *l*-alcohol, under which conditions the β -octyl group more or less completely displaces the methyl or ethyl group in the tartaric esters; (b) *d*- and *l*-tartaric acid were each treated in the same way with the two alcohols; (c) the β -octyl esters of the tartaric acids thus obtained were each hydrolysed partly with an insufficiency, or completely with an excess, of potassium hydroxide. In view of the experiments of Marekwald and McKenzie (*Ber.*, 1901,

* *d*-Methyl-*n*-nonylcarbinol, as now obtained by synthesis, has a higher positive rotation than the lævorotatory alcohol isolated by these investigators from the same oil.

† Methyl-*n*-decyl- and phenylmethyl-carbinols.

34, 469) on the varying velocity of esterification of an optically active acid with the two optical isomerides of an alcohol and the varying rate of hydrolysis of the corresponding esters, it was to be expected that such experiments carried out under many varied conditions (including those detailed by them) would yield a product of rotatory power different from $[\alpha]_D^{17} \pm 9.9^\circ$ if this were not the constant relating to optically pure methyl-*n*-hexylcarbinol. In no case, however, was a sample of the alcohol obtained as a result of these experiments of either lower or higher rotatory power.

Resolution of Fourteen Alcohols.

The resolution of fourteen alcohols is described in this section; twelve of these are of the general formula $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{R}$, where R represents the normal groups ethyl to undecyl, *isobutyl* and phenyl, whilst the other two have the formula $\text{C}_2\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{R}'$, where R' represents *n*-hexyl and phenyl. The preparation of these active alcohols has been repeated, and in all cases but two—methyl-*n*-decyl- and phenylmethyl-carbinol—the pure optically active alcohols have been obtained in at least two ways. In Figs.* 1 and 2 is illustrated the variation of the specific rotations with the temperature, and table II shows how in the series methyl-*n*-propyl- to methyl-*n*-undecyl-carbinol the molecular rotatory powers tend to approach a common value. These resolutions have been carried out by the method described (*loc. cit.*) for methyl-*n*-hexylcarbinol, that is, by the fractional crystallisation from acetone or aqueous acetone of the alkaloidal salts of either the hydrogen phthalic or succinic esters. Where a

TABLE II.

Specific and Molecular Rotatory Powers of the Dextrorotatory Alcohols.

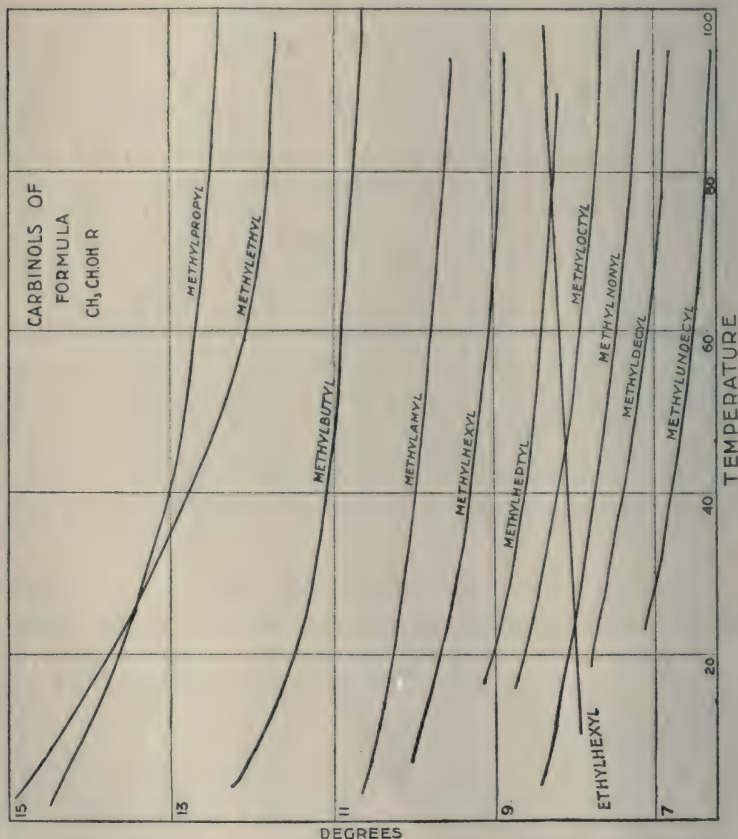
Alcohol.	$[\alpha]_D^{20}$	$[M]_D^{20}$	$[\alpha]_D^{50}$	$[M]_D^{50}$	$[\alpha]_{20}^{90}$	$[M]_{D1}^{90}$
Methylethylcarbinol	+13.87°	+10.3°	+12.48°	+9.2°	+11.84°	+8.8°
Methyl- <i>n</i> -propylcarbinol...	13.70	12.1	12.89	11.3	12.56	11.2
Methyl- <i>n</i> -butylcarbinol ...	11.57	11.8	11.02	11.2	10.90	11.1
Methyl- <i>n</i> -amylcarbinol ...	10.32	12.0	9.89	11.5	9.60	11.1
Methyl- <i>n</i> -hexylcarbinol ...	9.76	12.7	9.17	11.9	8.99	11.7
Methyl- <i>n</i> -heptylcarbinol ...	8.99	12.9	8.55	12.3	8.30	12.0
Methyl- <i>n</i> -octylcarbinol ...	8.68	13.7	8.14	12.9	7.80	12.3
Methyl- <i>n</i> -nonylcarbinol ...	8.13	14.0	7.66	13.2	7.28	12.5
Methyl- <i>n</i> -decylcarbinol ...	7.78	14.5	7.27	13.5	6.89	12.8
Methyl- <i>n</i> -undecylcarbinol .	7.22	14.4	6.67	13.3	6.39	12.7
Methyl <i>isobutyl</i> carbinol ...	20.54	20.9	19.25	19.6	18.32	18.7
Ethyl- <i>n</i> -hexylcarbinol	8.05	11.6	8.17	11.8	8.30	12.0
Phenylmethylcarbinol	42.86	52.3	42.68	52.1	41.60	50.8
Phenylethylcarbinol.....	27.73	37.7	32.52	44.2	35.54	48.3

* It should be noted that in Fig. 2 the scale of the ordinates is one-third that of the scale of the ordinates in Fig. 1.

resolution was effected, in all cases brucine formed the least soluble salt (*l*BdA) with the dextrorotatory hydrogen phthalic esters and the dextrorotatory hydrogen succinic esters of the two alcohols containing the phenyl group, whilst with the purely aliphatic alcohols this alkaloid formed the least soluble salt (*l*BdA) with the levorotatory

Fig. 1.

SPECIFIC ROTATORY POWER
AT DIFFERENT TEMPERATURES



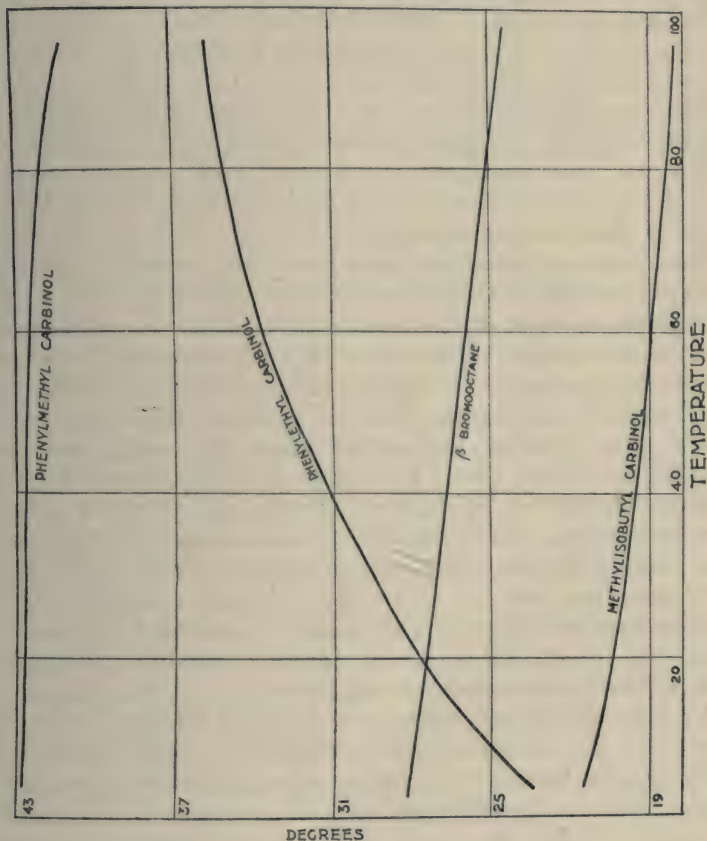
ester. Similar results were obtained with strychnine, whilst cinchonidine gave results of an opposite character, as with this alkaloid the least soluble salts were *l*BdA and *l*BdA in the case of the hydrogen phthalates and succinates respectively. Thus, for example, the following salts were found to be the least soluble component of the mixture of salts formed by neutralising the hydrogen ester with the

base: brucine and strychnine *d*- β -heptyl hydrogen phthalate, cinchonidine *l*- β -heptyl hydrogen phthalate, brucine *d*- δ -methyl- β -amyl hydrogen phthalate, brucine *l*- δ -methyl- β -amyl hydrogen succinate, and cinchonidine *l*-phenylethylcarbinyl hydrogen succinate.

Under the successful conditions employed in the other cases, no

FIG. 2.

SPECIFIC ROTATORY POWER
AT DIFFERENT TEMPERATURES



resolution was effected with the brucine, strychnine, or cinchonidine salts of the hydrogen phthalates of either phenylmethyl- or phenylethyl-carbinols, or with any salts of the hydrogen esters of tetrachlorophthalic acid.

In the optically pure state, none of the fourteen alcohols has previously been described, except methyl-*n*-heptylcarbinol, the lævo-

rotatory isomeride of which was isolated from oil of rue by Power and Lees (*loc. cit.*).

By fermentation methods, Combes and Le Bel (*Bull. Soc. chim.*, 1880, [ii], **33**, 106, 147; 1893, [iii], **9**, 676) obtained methylethyl- and methyl-*n*-butyl-carbinols with specific rotatory powers not exceeding $[\alpha]_D - 0.5^\circ$ and $[\alpha]_D - 8^\circ$ as against $[\alpha]_D^{20} + 13.87^\circ$ and $[\alpha]_D^{20} + 13.70^\circ$ respectively for the pure alcohols, whilst Meth (*Ber.*, 1907, **40**, 695) obtained methylethylcarbinol with $[\alpha]_D$ less than 1° by a method discussed in a former paper by one of us and Littlebury (*loc. cit.*). Marckwald (*Ber.*, 1905, **38**, 809) has also obtained phenylmethylcarbinol with $[\alpha]_D^{21} + 2.7^\circ$ (as against $[\alpha]_D^{21} + 42.87^\circ$) by the action of nitrous acid on *l*-phenylethylamine with $[\alpha]_D^{22} - 39.51^\circ$. Haller (*Compt. rend.*, 1910, **151**, 697) has quite recently isolated from coconut oil, feebly dextrorotatory forms of methyl-*n*-heptylcarbinol with $[\alpha]_D + 2.41^\circ$, and methyl-*n*-nonylcarbinol with $[\alpha]_D + 1.40^\circ$, lævorotatory specimens of these having been previously isolated from oil of rue by Power and Lees (*loc. cit.*).

The number of optically active alcohols here described is obviously too small to admit of any discussion of the results in so far as they affect the main object of the investigation. Attention, however, may be drawn to the following points. The rotatory powers of the series of alcohols described do not differ much in general character from some of the series of normal esters described by other investigators, as, for example, the series of the normal esters of diacetylglyceric acid (Frankland, *Trans.*, 1897, **71**, 270), where the rotatory powers gradually ascend to a maximum. Determinations of the molecular rotatory powers of the hydrogen phthalic esters in chloroform solution gave results* which run practically parallel with those of the alcohols in the pure state, although in the case of the esters the first member occupies apparently a normal place in the series and has not, as in the case of the alcohols (as also in so many series described by other investigators), an abnormal rotatory power.

At the outset of the investigation it was thought possible that amongst the alcohols of the type $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{R}$, some simple numerical relation might be found to exist among the numbers expressing the rotatory powers. It will be seen at once, however, that no comparison is feasible, if the influence of temperature be taken into account. Whilst the curves in Fig. 1 relating to the series (methylethylcarbinol excepted) become parallel as the temperature increases, yet at no temperature up to 100° (the limit of the present experiments†)

* See table, p. 63.

† The question as to a possible relation or constant existing at or above the boiling points of the alcohols for the molecular rotatory powers is reserved for further discussion when more material is available. The values of the rotatory

can the rotatory powers of the members of the series be compared with those of the alcohols of other types (see Fig. 2), or indeed with that of methylethylcarbinol.

The question of the (as yet unsolved) problem of the effect of association on the rotations of pure liquids (compare Walden, *loc. cit.*) naturally arises in this connexion. Does association account for the great differences in the temperature-coefficients as illustrated in Figs. 1 and 2? Now these alcohols as judged by Ramsay and Shields' capillarity ascension method or by Longinescu's empirical formula* (*Ann. Sci. Univ. Jassy*, 1903, 2, 126) are only slightly associated. Thus empirically the association factor for

<i>d</i> -Methylethylcarbinol	is 1.83	<i>d</i> -Methyl- <i>n</i> -nonylcarbinol	is 1.01
<i>d</i> -Methyl- <i>n</i> -propylcarbinol	„ 1.24	<i>d</i> -Ethyl- <i>n</i> -hexylcarbinol	„ 1.03
<i>d</i> -Methyl- <i>n</i> -butylcarbinol	„ 1.15	<i>d</i> -Methylisobutylcarbinol	„ 1.14
<i>d</i> -Methyl- <i>n</i> -amylcarbinol	„ 1.14	<i>d</i> -Phenylmethylcarbinol	„ 1.12
<i>d</i> -Methyl- <i>n</i> -hexylcarbinol	„ 1.08	<i>d</i> -Phenylethylcarbinol	„ 1.08
<i>d</i> -Methyl- <i>n</i> -heptylcarbinol	„ 1.05		

whilst, for example, by the capillarity ascension method *d*-methyl-ethylcarbinol between 19.8° and 36.8° has a mean association factor 1.8, and *d*-methyl-*n*-hexylcarbinol between 15° and 34° has 1.5.† Now the similarity of the temperature-coefficients for the alcohols in the series, despite the decrease in association as the molecular weight increases and the striking differences in the temperature-coefficients of phenylmethyl- and phenylethyl-carbinols, of methyl- and ethyl-*n*-hexylcarbinols, and of methylethylcarbinol and the rest of the series, seems to show that association has a very slight, if any, common influence on the rotation of these pure liquids. Since, however, it is a matter of some difficulty to measure small differences in association, the question of its influence on the rotatory powers of the individual alcohols could not be followed further.

The striking differences observed in the cases just mentioned in the variation of rotatory power with the temperature may be due partly to stereochemical causes, but possibly also to the more profound changes on the rotatory power of a complex, $R \cdot CH(OH) \cdot CH_2^-$, caused by hydrogen than by a radicle (CH_3).

Methylisobutylcarbinol was resolved at an early stage of the investigation to ascertain whether the differences in the rotatory powers of aliphatic alcohols corresponding with small differences in constitution were likely to be large. The exaltation in rotatory power powers of methyl-*n*-butyl- and methyl-*n*-octyl-carbinols commence to rise at about 125°, these being the only two alcohols investigated at the higher temperatures.

* $\frac{T}{100D} = \sqrt{n}$, where $T = b \cdot p$ on the absolute scale, $D = d_4^0$, and $n =$ the mean number of atoms in the molecule.

† It has often been observed that the capillarity ascension method gives higher values for the association factor than those obtained by empirical calculation.

caused by the *isobutyl* as compared with the *n-butyl* group is considerable, and affords additional evidence of powerful influence of constitution on rotatory power.

The halides corresponding with some of the alcohols have been prepared, the molecular rotatory powers being recorded in table III. In every case the conversion of the alcohol into a halide (Cl, Br or I) was accompanied by a change of sign in the rotation. Attempts to reconvert these halides into the optically pure alcohols have not as yet proved successful, and the preparation of them with any degree of certainty that racemisation has been avoided is tedious and very costly. This portion of the work has therefore not been extended for the present in case further physical measurements of the alcohols themselves appear desirable as the investigation proceeds. It will be noticed from Fig. 2 that the specific rotation of *d*- β -bromo-octane sinks regularly as the temperature increases, the curve being a straight line, and in this respect analogous among the alcohols only with ethyl-*n*-hexylcarbinol, for which, however, the specific rotation rises regularly with the temperature. The association factor for *d*- β -bromo-octane, calculated by Longinescu's formula, is 1.07.

The authors are greatly indebted to Dr. T. M. Lowry for the determinations of the refractive indices of the dextrorotatory alcohols as recorded in table IV. Dr. Lowry has also undertaken the determination of the magnetic and optical rotatory dispersion.* In respect to the optical rotatory dispersion a somewhat striking

TABLE III.
Rotatory Powers of the Halides.

	$[\alpha]_D^{25}$	$[M]_D^{25}$	$[\alpha]_D^{25}$	$[M]_D^{25}$
β -Iodobutane	-31.98°	-58.8°	—	—
β -Iodopentane	-37.15	-57.0	—	—
β -Iodohexane	-38.35	-80.9	—	—
β -Iodo-octane	-40.56	-90.4	+39.82°	+88.8°
γ -Iodononane	-17.50	-44.4	+17.65	+44.8
β -Bromo-octane	-27.47	-53.0	+27.53	+53.1
γ -Bromononane	-13.39	-27.7	+12.90	+26.7
β -Chloro-octane	-20.44	-30.4	+20.40	+30.3
γ -Chlorononane	-8.03	-13.0	+7.71	+12.5
α -Chloroethylbenzene ...	-5.80	-8.2	—	—
α -Chloropropylbenzene..	-3.87	-6.0	+3.79	6.0

connexion between this and the anomalous temperature-coefficients already mentioned has been observed. Thus, in a private communication, he states that those active alcohols of which the specific rotatory power varies normally with the temperature (see curves in Fig. 1 for methyl-*n*-propyl- to methyl-*n*-undecyl-carbinol) appear to give a constant value for the ratio $\alpha_{4879}/\alpha_{5461}$, which affords the most

* The results of these determinations will be published separately.

convenient measure of their rotatory dispersion; on the other hand, those alcohols which have a different temperature-coefficient of optical rotatory power (methylethyl-, ethyl-*n*-hexyl-, methyl*isobutyl*-, phenylmethyl-, and phenylethyl-carbinols) also differ in optical rotatory dispersion from the normal series, $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{R}$ (where $\text{R} = n\text{-C}_3\text{H}_7$ to $n\text{-C}_{11}\text{H}_{23}$), of active alcohols referred to above; there is, however, no simple relationship between the sign of the temperature-coefficient and the relative magnitude of the dispersion ratio.

TABLE IV.

Refractive Indices of the Dextrorotatory Alcohols.

Alcohol.	n_{D}^{20} .	d_4^{20} .	$\frac{n-1}{d} \cdot M$.	Difference for CH_2 .
Methylethylcarbinol	1.3954	0.8080	36.2	
Methyl- <i>n</i> -propylcarbinol	1.4053	0.8103	44.0	7.8
Methyl- <i>n</i> -butylcarbinol	1.4135	0.8150	51.8	7.8
Methyl- <i>n</i> -amylcarbinol	1.4209	0.8185	59.6	7.8
Methyl- <i>n</i> -hexylcarbinol	1.4256	0.8214	67.4	7.8
Methyl- <i>n</i> -heptylcarbinol.....	1.4299	0.8230	75.2	7.8
Methyl- <i>n</i> -octylcarbinol	1.4344	0.8250	83.1	7.9
Methyl- <i>n</i> -nonylcarbinol	1.4369	0.8270	91.0	7.9
Methyl- <i>n</i> -decylcarbinol	1.4423	0.8315	99.0	8.0
Ethyl- <i>n</i> -hexylcarbinol.....	1.4308	0.8260	75.1	
Phenylmethylcarbinol.....	1.5211	1.0135	63.7	
Phenylethylcarbinol	1.5200	0.9940	71.1	7.4
Methyl <i>isobutyl</i> carbinol	1.4103	0.8077	51.8	

It is believed that the present paper shows that synthetical methods may be used to obtain accurate comparative values of the rotatory powers of optically active alcohols. It is hoped that the further investigation of several other series of alcohols and also of acids of similar constitution may give values which will be capable of easier interpretation in a quantitative manner than the results of those investigators who have preceded the present authors in this field.

EXPERIMENTAL.

The Racemic Alcohols.

Of the fourteen racemic secondary alcohols which have been investigated, thirteen* have been prepared either by the interaction of an aldehyde and a Grignard reagent, or by the reduction of the corresponding ketone in aqueous alcoholic solution with sodium.

The reactions between acetaldehyde and magnesium ethyl bromide, magnesium propyl bromide (or chloride), and magnesium *isobutyl* bromide respectively; between *n*-heptaldehyde and magnesium ethyl bromide; between *n*-octaldehyde and magnesium methyl iodide, and

* Methyl-*n*-hexylcarbinol is obtained commercially by the distillation of a castor oil soap with sodium hydroxide.

between benzaldehyde and magnesium methyl and ethyl iodides all proceed smoothly, and were carried out in the usual manner, the cheaper reagent being used in slight excess. In this way 50 to 70 per cent. yields were obtained of crude methylethylcarbinol (b. p. 92—99°),* methyl-*n*-propylcarbinol (b. p. 118—122°),† methylisobutylcarbinol (b. p. 125—132°),‡ ethyl-*n*-hexylcarbinol (b. p. 118—121°/65 mm.), methyl-*n*-heptylcarbinol (b. p. 91°/12 mm.), phenylmethylcarbinol (b. p. 100°/18 mm.),‡ and phenylethylcarbinol (b. p. 105—108°/10 mm.).‡

The reaction between magnesium *n*-butyl iodide and acetaldehyde gave only about 10 per cent. of the calculated yield of methyl-*n*-butylcarbinol (b. p. 136°), whilst methyl-*n*-heptylcarbinol and methyl-*n*-octylcarbinol form a very small proportion of the products formed by the reactions between acetaldehyde and magnesium *n*-heptyl and *n*-octyl iodides.

The *n*-octaldehyde used was prepared from *n*-octyl alcohol by Sabatier's excellent method for the conversion of primary alcohols into the corresponding aldehydes. The alcohol was heated in a flask, which was surrounded by a metal-bath kept at 200°. A rapid current of pure hydrogen passing through this flask carried the alcohol to a glass tube of which 50 cm. were packed with pumice stone covered with finely divided copper, and which was heated to 300—315°. The aldehyde was washed out of the condensed products by a solution of sodium hydrogen sulphite, and the process repeated four times with the unconverted alcohol. The *sodium hydrogen sulphite* compound of *n*-octaldehyde was crystallised from aqueous alcohol, and obtained in nacreous leaflets, which did not melt below 270°. Decomposition of this compound with a strong solution of sodium carbonate, distillation of the product in a current of steam, and subsequent rectification gave a 50 per cent. yield (calculated from the alcohol used) of *n*-octaldehyde (b. p. 77°/23 mm.). No by-products were observed in this preparation, the loss being due very largely to inefficient condensation of the products carried over by the hydrogen.

The ketones required, $\text{CH}_3\cdot\text{CO}\cdot\text{R}$, were prepared by passing the various acids, $\text{R}\cdot\text{CO}_2\text{H}$, mixed with five to seven times their weight of glacial acetic acid, over thorium oxide heated to 400° (Senderens, *Compt. rend.*, 1909, 149, 995 *et seq.*). The thoria was mixed with glass wool and loosely packed into a tube of Jena glass heated for 50 cm. of its length. The normal acids used were hexoic, nonoic,

* Methylethylcarbinol requires careful and repeated fractionation to separate it from ether.

† Both of these crude alcohols contained paracetaldehyde.

‡ Each of these alcohols had a peculiar characteristic and pungent odour, which was not removed by repeated distillation, but was not present in the optically active isomerides.

undecic, and lauric acid. The solutions of these in acetic acid were passed through the slightly inclined tube from a dropping funnel at an hourly rate of about 50 c.c. In each case the products were practically neutral, and no charring took place in the heated tube. Fractional distillation of the products gave from 70 to 90 per cent. yields (calculated from the weight taken of the acids named) of the ketones of the general formula $\text{CH}_3\cdot\text{CO}\cdot\text{R}$, and from 30 to 10 per cent. yields of the ketones with the formula $\text{R}\cdot\text{CO}\cdot\text{R}$. The methyl *n*-amyl ketone prepared in this manner was identical with a sample of the same compound purchased from Schuchardt, which had been prepared by the distillation of a mixture of barium hexoate and acetate. Some properties of the ketones prepared are set out in table V.

TABLE V.

Ketone.	Melting point.	Boiling point.	Melting point of semicarbazone.*
Methyl <i>n</i> -amyl ketone	—	150°	123·0°
Methyl <i>n</i> -octyl „	—	210	121·5
Methyl <i>n</i> -decyl „	20°	144°/11 mm.	122—123
Methyl <i>n</i> -undecyl „	29	160°/16 mm.	126·0
Diamyl „	—	223°	—
Dioctyl „	53	—	—
†Didecyl „	64	—	—
Diundecyl „	70—71	—	—

* All obtained from aqueous alcohol in the form of prismatic needles.

† The oxime of this ketone crystallises from aqueous needles in hair-like needles, which melt at 27·5°, and readily regenerates the ketone when boiled with dilute hydrochloric acid.

It will be seen that the semicarbazones are of little value for the characterisation of the ketones, $\text{CH}_3\cdot\text{CO}\cdot\text{R}$, for these all melt at about 123°, whilst the ketones, $\text{R}\cdot\text{CO}\cdot\text{R}$ (where R contains more than five carbon atoms), do not form semicarbazones by the ordinary methods for the preparation of these compounds.

The nonoic and undecic acids used in the preparation of the above-mentioned ketones were obtained in almost quantitative yields* by Darzens' method (*Compt. rend.*, 1907, 144, 329), in which the ethyl esters of Δ^1 -nonylenic acid† and commercial undecenoic acid were reduced by hydrogen in the presence of finely divided nickel heated to 180°.

* Thus, for example, in one set of experiments 300 grams of undecenoic acid were esterified and reduced. After hydrolysis of the resulting saturated ester and distillation of the acid, 260 grams of undecic acid (m. p. 28°) were obtained. From this was prepared 174 grams of methyl *n*-decyl ketone along with a quantity of didecyl ketone, 43 grams of the acid being recovered; 133 grams of methyl-*n*-decyl-carbinol were obtained by the reduction of this ketone.

† Δ^1 -Nonylenic acid was prepared by the excellent method of Harding and Weizmann (*Trans.*, 1910, 97, 299).

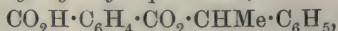
The ketones of the general formula $\text{CH}_3\cdot\text{CO}\cdot\text{R}$, as described above, and also methyl *n*-butyl ketone and methyl *n*-nonyl ketone (purchased from Kahlbaum) were reduced in alcoholic solution by means of sodium, the procedure of Thoms and Mannich (*Ber.*, 1903, 36, 2544) adopted for their reduction of methyl *n*-nonyl ketone being followed. The alcohols* thus obtained were (the yields varying from 70–80 per cent.): methyl-*n*-butylcarbinol (b. p. 136°), methyl-*n*-amylcarbinol (b. p. 158–160°), methyl-*n*-octylcarbinol (b. p. 210–211°), methyl-*n*-nonylcarbinol (b. p. 119°/12 mm.), methyl-*n*-decylcarbinol (m. p. about 5°, b. p. 140°/15 mm.), and methyl-*n*-undecylcarbinol (b. p. 151°/11 mm.).

The Racemic Hydrogen Phthalic Esters.

The hydrogen phthalic esters were prepared by heating the alcohols with phthalic anhydride (equal mols.) for about ten hours at 115° in an oil-bath, except in the case of methylethyl- and methyl-*n*-propyl-carbinols, which were heated on a water-bath. The products, which generally contained some phthalic acid and unaltered anhydride, were poured when cold into a solution of sodium carbonate. After keeping for some hours to allow of the hydrolysis of any anhydride, the alkaline solutions were extracted three times with ether to remove unesterified alcohols and neutral phthalic esters, both of which dissolve to a considerable extent in aqueous solutions of the sodium alkyl phthalates.* The acid esters were then precipitated by hydrochloric acid, either as oils or solids of low melting point, and were extracted with chloroform. Phthalic acid, being insoluble in dry chloroform, is thus readily removed, whilst the dried extracts after complete removal of the chloroform, at first on a water-bath, and finally under diminished pressure, consisted of the hydrogen phthalates in the form of opaque, crystalline masses. These acid esters are very soluble in all the common organic media, but some of them crystallise readily from light petroleum. The melting points of the racemic hydrogen phthalates are recorded in table IX, p. 63, along with those of the corresponding active compounds, whilst the composition and purity of each were checked by titration in alcoholic solution with sodium hydroxide.

The following compounds were also obtained:

Phenylmethylcarbinyl hydrogen phthalate,

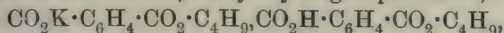


which crystallises in opaque leaflets from either glacial acetic acid or benzene, and melts at 108°.

* All these alcohols were comparatively much purer than those obtained by the Grignard reactions.

† Such solutions cannot be warmed to 70° or above without undergoing some decomposition.

An acid potassium salt of β -butyl hydrogen phthalate,



which crystallises from acetone in very slender needles, melts at $166\text{--}168^\circ$, and is decomposed by warm water.

Found, $\text{K} = 8.07$. $\text{C}_{24}\text{H}_{27}\text{O}_8\text{K}$ requires $\text{K} = 8.09$ per cent.

The Racemic Hydrogen Succinates.

Several acid esters of succinic acid were prepared by a method similar to that employed for the corresponding phthalates. They are, however, best extracted by ether instead of chloroform, traces of succinic acid being readily removed from the ethereal solutions by washing with water. The following carbinols gave hydrogen succinates in the form of viscous oils which did not solidify when kept at -10° : methylethyl-, methyl-*n*-propyl-, methyl-*n*-butyl-, methyl-*n*-nonyl-, methylisobutyl-, and phenylethyl-carbinols, whilst that of phenyl-methylcarbinol crystallises from light petroleum in beautiful nacreous leaflets, and melts at $60\text{--}61^\circ$.

Brucine Salts of the Acid Esters.

The method adopted in each case for the preparation of the pure brucine salt of the dextrorotatory acid ester was: A solution of pure* racemic acid ester in acetone is boiled with the calculated amount (equal mols.) of brucine,† which is added in small portions at a time until the alkaloid is completely dissolved. The solution, having been filtered (if necessary) while warm, is then concentrated, and set aside in the ice-chest for some hours. The crop of crystals is collected and recrystallised several times under the same conditions. The first mother liquor when acidified yields a lævorotatory acid ester, and is used for the preparation of the pure lævorotatory alcohol, whilst that from the first recrystallisation yields an acid ester, which is usually slightly dextrorotatory, and can be conveniently used for the preparation of the strychnine salt of the pure dextrorotatory acid ester. The melting points and rotation of the brucine salts become constant after three to ten crystallisations, whilst in most cases the solubility in warm acetone decreases to a considerable extent as the salt becomes pure. The actual solubility of the pure salts of the phthalates varies considerably and most irregularly even in the homologous series described (see table VI); thus, for example, in the case of the member of the series corresponding with octane, 100 grams of the pure brucine salt would require about 10 litres of hot acetone to dissolve it,

* The success of the resolution largely depends on the purity of the acid ester.

† All the alkaloids mentioned in this paper were the purest commercial specimens supplied by Merck, and were recovered unchanged in rotation.

whilst the same quantity of the salt of that corresponding with nonane would require less than half a litre. The composition of the brucine salts, as well as of the other alkaloidal salts described in this paper, was determined by an estimation of the nitrogen content. In every case, as was to be expected, the salt contained one molecule of each component. The brucine salts of the acid esters of succinic acid are, as a rule, much more soluble in acetone than the salts of the corresponding phthalates. The following salts were also prepared : *Dibrucine phthalate*, $C_{54}H_{58}O_{12}N_4$, which crystallises from warm alcohol in glistening lamellæ, which melt and decompose at 113° , and are very slightly soluble in cold alcohol or chloroform. *Brucine hydrogen phthalate*, $C_{31}H_{32}O_8N_2$, which crystallises from alcohol in clusters of prismatic needles, melts at 216° , and when dissolved in chloroform has $[\alpha]_D + 13.52^\circ$. *Brucine hydrogen succinate*, $C_{27}H_{32}O_8N_2$, crystallises from aqueous alcohol in needles, melts at $217-219^\circ$, and in absolute ethyl alcohol has $[\alpha]_D - 17.70^\circ$.

TABLE VI.

Brucine Salts.

Brucine salt of the <i>hydrogen phthalate</i> of	Melting point.	Rotatory power* in ethyl alcohol.	
		Specific.	Molecular.
<i>d</i> -Methylethylcarbinol	154—155°	-2.93°	-18.1°
<i>d</i> -Methyl- <i>n</i> -propylcarbinol	154—155	-3.91	-24.6
<i>d</i> -Methyl- <i>n</i> -butylcarbinol	144—145	4.04	26.0
<i>d</i> -Methyl- <i>n</i> -amylcarbinol	137—138	4.42	29.1
<i>d</i> -Methyl- <i>n</i> -hexylcarbinol	151	5.44	36.6
<i>d</i> -Methyl- <i>n</i> -heptylcarbinol	140—142	4.97	34.1
<i>d</i> -Methyl- <i>n</i> -octylcarbinol	136—138	6.01	42.1
<i>d</i> -Methyl- <i>n</i> -nonylcarbinol	113—116	5.22	37.2
<i>d</i> -Methyl- <i>n</i> -decylcarbinol	123—124	6.06	44.1
<i>d</i> -Methyl- <i>n</i> -undecylcarbinol ...	120—122	5.69	42.2
<i>d</i> -Methylisobutylcarbinol	167—168	4.19	26.9
<i>d</i> -Ethyl- <i>n</i> -hexylcarbinol	108—110	11.41	78.5
<i>hydrogen succinate</i> of			
<i>d</i> Phenylmethylcarbinol	110.5	+15.33	+94.4
<i>d</i> -Phenylethylcarbinol	103—105	16.28	100.2
<i>l</i> -Methylisobutylcarbinol	95	-22.41	-133.6

* In all cases mentioned in this paper where the rotatory power of a compound has been observed in solution, the solution was prepared by making up 1 gram of the compound to 20 c.c. with the solvent.

Cinchonidine and Strychnine Salts of the Acid Esters.

The cinchonidine salts of the acid esters were prepared, as a rule, in the same way as the brucine salts, but when dissolved in hot acetone they often decompose and deposit the alkaloid. It was found preferable in some cases to adopt the following method, which was employed for the preparation of the strychnine salts : Equimolecular proportions

of the alkaloid and the acid ester are dissolved in chloroform; the chloroform is then distilled off, and whilst the salt is still in the pasty condition, it is dissolved by the addition of the requisite amount of boiling acetone. For each recrystallisation the salt is dissolved in chloroform, and a like procedure followed.

Most of the cinchonidine salts are very soluble in acetone, and do not crystallise at all readily from aqueous acetone. The strychnine salts of the optically pure acid esters are only very slightly soluble in cold acetone, and are always partly decomposed when boiled with acetone. The strychnine salts described in table VIII were all prepared from samples of acid esters possessing a slight positive rotation. Strychnine salts of the *dl*-hydrogen phthalates were unaltered in rotation by recrystallisation in the manner described, whilst the rotation of the strychnine salt of a partially active hydrogen phthalate of phenylmethylecarbinol was not affected by crystallisation.

TABLE VII.
Cinchonidine Salts.

Cinchonidine salt of the <i>hydrogen phthalate</i> of	Melting point.	Rotation in ethyl alcohol.	
		Specific.	Molecular.
<i>l</i> -Methyl- <i>n</i> -amylcarbinol	108—109°	-70·36°	-392·6°
<i>l</i> -Methyl- <i>n</i> -hexylcarbinol	112—116	68·02	389·0
<i>l</i> -Ethyl- <i>n</i> -hexylcarbinol.....	115—118	60·47	354·3
<i>hydrogen succinate</i> of			
<i>d</i> -Methyl- <i>n</i> -butylcarbinol	89— 90	76·73	380·6
<i>d</i> -Methylisobutylcarbinol	100—102	76·54	379·6
<i>l</i> -Phenylethylcarbinol	161—162	118·46	628·2

TABLE VIII.
Strychnine Salts.

Strychnine salt of the <i>hydrogen phthalate</i> of	Melting point.	Rotation in chloroform.	
		Specific.	Molecular.
<i>d</i> -Methylethylcarbinol.....	149—152°	-20·04°	-27·8°
<i>d</i> -Methyl- <i>n</i> -propylcarbinol	179—181	-18·56	30·7
<i>d</i> -Methyl- <i>n</i> -amylcarbinol	203—204	-18·89	31·7
<i>d</i> -Methyl- <i>n</i> -hexylcarbinol	180	-18·74	32·7
<i>d</i> -Methyl- <i>n</i> -heptylcarbinol	142—143	-19·47	32·2
<i>d</i> -Methyl- <i>n</i> -octylcarbinol.....	136—137	-18·37	34·3
<i>d</i> -Methyl- <i>n</i> -nonylcarbinol	144—145	-17·11	38·2
<i>d</i> -Methyl- <i>n</i> -undecylcarbinol	142—143	-18·69	36·6

*Optically Active Acid Esters of the Alcohols.**

The optically active acid esters were readily obtained from the brucine and cinchonidine salts when alcoholic solutions of these were

* Attempts were made to resolve the hydrogen tetrachlorophthalic esters of methylethyl-, methylisobutyl-, methyl-*n*-propyl-, and methyl-*n*-butyl-carbinols by fractional crystallisation of the brucine and cinchonidine salts, but in no case was any resolution effected under the conditions tried.

poured into dilute hydrochloric acid. Although the oily esters, which were at once precipitated, in many cases solidified to crystalline masses, it was generally found necessary to dissolve them in ether, so that by repeated washing with very dilute hydrochloric acid the hydrochloride of the alkaloid could be completely removed. The strychnine salts were decomposed in a somewhat different manner. Alcoholic solutions of these were poured into dilute ammonia, and, after the strychnine had been removed by filtration, the acid esters were obtained on the addition of hydrochloric acid.

The acid phthalic esters (see table IX) were all obtained as crystalline masses after removal of the solvent, and in some cases are readily recrystallised from light petroleum, but, like the acid succinic acids and all the corresponding racemic compounds, they are very soluble in the common organic media. The optically active acid succinic esters were only isolated in three cases, being usually hydrolysed at once. They are all oils, which decompose when distilled, so that the observed rotatory powers may be misleading, as the solvent (ether) may not have been completely removed. The hydrogen succinate of *d*-methylisobutylcarbinol had $[\alpha]_D + 14.52^\circ$ in chloroform, and the corresponding lævo-compound, $[\alpha]_D - 14.37^\circ$; *d*- β -hexyl hydrogen succinate had $[\alpha]_D + 6.19^\circ$ in chloroform, whilst the hydrogen succinate of phenylethylcarbinol had $\alpha - 20.06^\circ$ in a 25-mm. tube.

The Optically Active Alcohols.

The alcohols, except in the case of methylethyl- and methyl-*n*-undecyl-carbinols, were obtained by the following method: The acid ester is dissolved in a hot concentrated aqueous solution of potassium hydroxides ($2\frac{1}{2}$ mols.), and the alcohol formed by the hydrolysis is distilled over in a current of steam. It is then extracted from the distillate by ether, and the ethereal solution is dried by long keeping over freshly ignited potassium carbonate.

The optically active alcohols obtained were comparatively stable in the presence of alkali hydroxides. Although as a matter of precaution they were removed from the prolonged action of potassium hydroxide as rapidly as possible by a current of steam during the hydrolysis, yet in two or three cases (notably those of methyl-*n*-hexyl- and methyl-*n*-undecyl-carbinols) by actual experiment it was found that the rotation was unaltered by continued boiling under a reflux condenser with aqueous alkalis. The alcohols were obtained as colourless, strongly refracting liquids or low melting solids. They have faint characteristic odours, in all cases these being far less than those of the optically inactive isomerides. There seems to be in some cases, for

TABLE IX.
The Hydrogen Phthalic Esters.

Hydrogen phthalate of	Melting point of		Rotations in chloroform.		Rotations in ethyl alcohol.		Origin of ester. †
	Racemic.	Active.	[α] _D	[M] _D	[α] _D	[M] _D	
Methylethylcarbinol	56—57°	*46—47°	+33·54°	+74·5°	+38·97°	+86·5°	B
Methyl <i>n</i> -propylcarbinol	—	—	+33·51	+74·4	—	—	S
Methyl <i>n</i> -butylcarbinol	*60—61	*34	+36·94	+87·2	—	—	S
Methyl <i>n</i> -amylcarbinol ..	57—58	76·5	+43·39	+108·5	+47·02	+117·5	B
.....	—	—	+43·89	+115·9	+48·64	+128·4	B
.....	—	—	+43·94	+116·0	—	—	S
.....	—	—	-43·81	-115·7	-48·52	-128·0	C
Methyl <i>n</i> -hexylcarbinol ..	55	75	+42·94	+119·3	+48·08	+133·7	B
.....	—	—	-43·27	-120·3	-48·26	-134·2	C
Methyl <i>n</i> -heptylcarbinol ..	*42—44	58—59	+41·17	+120·1	+46·06	+134·5	B
.....	—	—	+41·04	+119·9	—	—	S
Methyl <i>n</i> -octylcarbinol ..	*48—49	*38—39	+39·01	+119·3	+45·19	+138·3	B
.....	—	—	+39·11	+119·7	—	—	S
Methyl <i>n</i> -nonylcarbinol ..	*49—50	*31—32	+37·34	+119·5	—	—	B
.....	—	—	+37·19	+118·8	+44·29	+141·4	S
Methyl <i>n</i> -decylcarbinol ..	50—51	*28	+35·59	+121·0	+43·41	+143·9	B
.....	58—59	*26	+35·54	+124·0	+41·13	+143·1	B
Methyl <i>n</i> -undecylcarbinol ..	—	—	+35·13	+122·3	—	—	S
.....	—	—	+13·78	+19·9	+19·40	+27·9	B
Ethyl <i>n</i> -hexylcarbinol	47—49	54—55	-13·62	-19·6	-19·45	-28·0	C

* Denotes a melting point determined of the crystalline mass drained on a porous tile without recrystallisation.

† B denotes from brucine salt; S from strychnine salt, and C from cinchonidine salt.

example, phenylethylcarbinol, a slight difference in the aroma of the dextrorotatory and levorotatory forms.

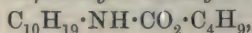
Specimens of some of the alcohols of each type described were found to be unaltered in rotatory power after exposure to light for many months whilst stored in common glass bottles. Several of them were reconverted into the hydrogen phthalic esters, these being readily obtained without recrystallisation with the maximum rotation observed, showing that at least these alcohols will not undergo racemisation when removed from natural products by the "phthalic anhydride" method (compare Haller, *Compt. rend.*, 1910, 151, 697). At least 30 c.c. of each of the active alcohols mentioned below have been obtained and the preparations repeated. The densities have been determined in a pycnometer holding 3.5 c.c., and the rotations in jacketed tubes of 50 and 100 mm. long.

Methylethylcarbinol.—Since this alcohol is very difficult to separate from ether, it was "salted out" of the distillate obtained from the hydrolysis of the hydrogen phthalic ester by means of potassium carbonate. Specimens of the dextrorotatory alcohol obtained from the brucine and strychnine salts of this acid ester agreed in rotatory power, this being unaltered by keeping over freshly-ignited barium oxide.

The dextrorotatory alcohol boiled at $99^{\circ}/760$ mm., had $d_{4}^{15.6}$ 0.8106, d_{4}^{27} 0.8025, $d_{4}^{61.6}$ 0.7717, and $d_{4}^{77.5}$ 0.7566; and $[\alpha]_D +14.83^{\circ}$ at 4.5° , $+14.03^{\circ}$ at 17.8° , $+13.52^{\circ}$ at 27° , $+13.08^{\circ}$ at 36.5° , $+12.57^{\circ}$ at 48.7° , $+12.15^{\circ}$ at 58° , $+11.77^{\circ}$ at 72° , and $+11.83^{\circ}$ at 91.7° .

The alkaloidal salts of the *l*- β -butyl hydrogen phthalate and of the corresponding succinates crystallise badly, and are decomposed when warmed with acetone.

Several attempts have been made by one of us and W. O. Littlebury to resolve this alcohol by the "menthylcarbimide" method (see *Trans.*, 1906, 89, 465, 1254). *dl*- β -Butyl *l*-menthylcarbamate,



was readily obtained by warming equimolecular quantities of the carbinol and *l*-menthylcarbamide. It crystallises in large prismatic tablets, which melt at 54° , and have $M_D - 162.4$ in chloroform.

When recrystallised several times from aqueous ethyl alcohol, the melting point rose to 71° , and the molecular rotatory power fell to -152.4° . The resolution, however, was not complete, as *d*- β -butyl *l*-menthylcarbamate, prepared from the dextrorotatory alcohol described above, melted at 72° , and had $[\alpha]_D - 55.78^{\circ}$ and $M_D - 142.2^{\circ}$ in chloroform. Experiments in this direction were not completed, as it was found impossible to hydrolyse the carbamate except by means of alcoholic potassium hydroxide, and then the separation of the carbinol from the ethyl (or methyl) alcohol used required too much material.

l- β -Iodobutane.—Several comparative experiments were carried out to determine the conditions for displacing the hydroxyl group of the carbinol by iodine without racemisation of the compounds. The product of highest lævorotatory power was obtained when the dextro-rotatory alcohol was saturated at 0° with hydrogen iodide (free from iodine) and warmed in a sealed tube for thirty minutes at a temperature not exceeding 60°. The lævorotatory iodo-compound thus prepared boiled at 118°, had d_4^{17} 1.5970, and $[\alpha]_D^{17}$ -31.98°. Attempts to convert this iodide into optically active methylethylcarbin-carbinol (*sec.*-butylcarbinol) by successive treatment with magnesium (in ethereal solution) and formaldehyde (trioxymethylene) gave negative results; under the conditions tried, the products were always optically inactive, racemisation probably taking place during the formation of the Grignard reagent.

d-Methyl-*n*-propylcarbinol.—This alcohol, prepared either from the brucine or the strychnine salt of the dextrorotatory hydrogen phthalic ester, boiled at 118.5—119.5°. Determinations of the density gave $d_4^{12.3}$ 0.8169, $d_4^{26.8}$ 0.8058, $d_4^{36.8}$ 0.7967, $d_4^{47.3}$ 0.7871, $d_4^{60.5}$ 0.7751; and of the specific rotatory power: $[\alpha]_D^{17}$ +14.38°, +13.86° at 19°, +13.44° at 27.5°, +13.14° at 38°, +12.91° at 49°, +12.79° at 58.5°, +12.55° at 73°, and +12.56° at 90.5°.

l- β -Iodopentane.—This compound was prepared as follows: The dextrorotatory alcohol was saturated with pure hydrogen iodide at 0°, and heated at 100° in a sealed tube for thirty minutes. After purification in the usual manner, the iodide boiled at 143°, had d_4^{17} 1.5067, and $[\alpha]_D^{17}$ -37.15°.

d-Methyl-*n*-butylcarbinol, of identical rotatory power, was obtained from the brucine salt of the dextrorotatory hydrogen phthalic ester and from the cinchonidine salt of the dextrorotatory hydrogen succinic ester. It boiled at 137—138°, had $d_4^{16.8}$ 0.8179, $d_4^{37.5}$ 0.8021, $d_4^{50.3}$ 0.7903, $d_4^{71.0}$ 0.7726, and d_4^{133} 0.7134, and $[\alpha]_D^{17}$ +12.08°, +11.60° at 19°, +11.45° at 26.8°, +11.27° at 35.7°, +11.05° at 48°, +10.87° at 59°, +10.77° at 72°, +10.77° at 93°, and +11.28° at 133°.

l- β -Iodohexane was prepared in a similar manner to the corresponding pentane derivative. It had d_4^{17} 1.4354, and $[\alpha]_D^{17}$ -38.35°.

d-Methyl-*n*-amylcarbinol.—This alcohol boiled at 73.5°/20 mm., had d_4^{20} 0.8190, d_4^{35} 0.8050, d_4^{61} 0.7920, d_4^{64} 0.7815, and $[\alpha]_D^{25}$ +10.21°, +10.14° at 31°, +9.95° at 46°, and +9.75° at 69.3°.

l-Methyl-*n*-amylcarbinol had very similar constants to the dextro-rotatory alcohol. It boiled at 74.5°/23 mm., had d_4^{20} 0.8184, and $[\alpha]_D^{34}$ -10.52°, -10.48° at 17°, and -9.58° at 91°.

d- and *l*-Methyl-*n*-hexylcarbinols.—These alcohols (Pickard and Kenyon; *loc. cit.*) have been prepared in larger quantities than any of the other alcohols here described. The following additional

constants have been determined for the dextrorotatory compound: d_4^{25} 0.8170, d_4^{35} 0.8095, d_4^{46} 0.8019, and $[\alpha]_D +10.00^\circ$ at 9° , $+9.51^\circ$ at 25.5° , $+9.40^\circ$ at 35.5° , $+9.19^\circ$ at 48° , and $+8.98^\circ$ at 91.5° .

dl-Methyl-n-hexylcarbinol.—Several investigators have observed that ordinary commercial methylhexylcarbinol (*sec*-octyl alcohol) possesses a slight rotatory power. Samples supplied by Kahlbaum had $\alpha^{17} -0.15^\circ$ in a 2-dcm. tube. This alcohol was converted into the hydrogen phthalic ester, and recrystallised twice from glacial acetic acid and once from light petroleum. The alcohol recovered from this purified ester possessed approximately the same rotatory power. It was therefore assumed that the commercial alcohol contained a small amount of the *l*-alcohol. To it was then added the calculated amount of the *d*-alcohol, so that an inactive product was obtained. This was treated with phthalic anhydride, and the ester purified as before. The alcohol prepared by the hydrolysis of this thrice-recrystallised ester was found to be completely inactive. The experiments described below, in which an inactive methylhexylcarbinol was used, were carried out with a product prepared in this way.

Esters of Methyl-n-hexylcarbinol.

d- β -Octylacetate, $\text{CH}_3 \cdot \text{CO}_2 \cdot \text{CHMe} \cdot \text{C}_6\text{H}_5$.—This was obtained as a pleasant-smelling, mobile liquid, boiling at $86\text{--}88^\circ/22$ mm. It had d_4^{17} 0.8569, and $[\alpha]_D^{17} +7.65^\circ$, whilst when hydrolysed with potassium hydroxide it gave the optically pure *d*-alcohol.

d- β -Octyl β -phenylpropionate, $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{CHMe} \cdot \text{C}_6\text{H}_{13}$.—The acid was converted into the chloride by heating on the water-bath with the calculated amount of thionyl chloride. The product was then warmed with the *d*-alcohol until hydrogen chloride ceased to be evolved. The oily ester was then purified in the usual manner, and it was found that redistillation did not alter its rotatory power:

0.1176 gave 0.3354 CO_2 and 0.1036 H_2O . $\text{C} = 77.78$; $\text{H} = 9.80$.

$\text{C}_{17}\text{H}_{26}\text{O}_2$ requires $\text{C} = 77.86$; $\text{H} = 9.92$ per cent.

The ester is a transparent and odourless liquid of somewhat viscous character, which boils at $192\text{--}196^\circ/27$ mm., and has d_4^{17} 0.9483. The rotation observed in a 1-dcm. tube gave $\alpha_D +11.56^\circ$, whence $[\alpha]_D^{17} +12.19^\circ$. A second preparation, made by the method of saturating a solution of the acid in the *d*-alcohol with hydrogen chloride, had $[\alpha]_D^{17} +12.26^\circ$.

The corresponding *laevo*-compound was prepared in a similar manner by the first of the methods indicated above. It boils at $200\text{--}202^\circ/32$ mm., and has d_4^{17} 0.9476. In a 1-dcm. tube it gave $\alpha_D -11.85^\circ$, whence $[\alpha]_D^{17} -12.51^\circ$. From each of these two esters there were

recovered, by hydrolysis, alcohols with $[\alpha]_D^{17} \pm 9.9^\circ$. The corresponding inactive ester boils at $190\text{--}192^\circ/27$ mm., and has $d_4^{17} 0.9815$.

Esters of Cinnamic Acid.—These were prepared by passing hydrogen chloride for forty-five minutes through a mixture of equivalent proportions of the alcohols and cinnamic acid, which was kept at 110° . The esters were purified in the usual manner, and were obtained as clear, colourless liquids without odour.

The *d*- β -octyl cinnamate thus prepared boiled at $218^\circ/28$ mm., had $d_4^{17} 0.9694$, and in a 50-mm. tube $\alpha^{17} + 19.48^\circ$, whence $[\alpha]_D^{17} + 40.19^\circ$. The alcohol recovered from this ester had $[\alpha]_D^{20} + 9.66^\circ$. The ester, which was quite free from chlorine, when repeatedly treated with aluminium amalgam in moist ethereal solution was quantitatively converted into the corresponding ester of β -phenylpropionic acid, which had $[\alpha]_D^{17} + 12.36^\circ$.

The corresponding *laevo*-ester boiled at $211^\circ/23$ mm., had $d_4^{17} + 0.9692$, and $[\alpha]_D^{17} - 39.78^\circ$, whilst the *dl*-ester boiled at $213^\circ/28$ mm., and had $d_4^{17} 0.9715$:

0.1261 gave 0.3620 CO_2 and $0.1065 \text{ H}_2\text{O}$. $\text{C} = 78.51$; $\text{H} = 9.38$.

$\text{C}_{17}\text{H}_{24}\text{O}_2$ requires $\text{C} = 78.46$; $\text{H} = 9.23$ per cent.

Esters of Phenylpropionic Acid.—The esters of phenylpropionic acid were prepared in the same manner as those of cinnamic acid. They were obtained free from chlorine, and when hydrolysed gave the optically pure alcohols. They are colourless, highly refractive liquids, which possess faint odours. The *d*-ester boiled at $206\text{--}208^\circ/20$ mm., had $d_4^{17} 0.9823$, and in a 50-mm. tube gave $\alpha^{17} + 24.95^\circ$, whence $[\alpha]_D^{17} + 50.80^\circ$. Repeated treatment with aluminium amalgam in moist ethereal solution converted the unsaturated ester into the corresponding derivative of β -phenylpropionic acid, which had $[\alpha]_D^{17} + 12.06^\circ$. The *l*-ester boiled at $209^\circ/27$ mm., had $d_4^{17} 0.9719$, and gave $\alpha^{17} - 12.33^\circ$ in a 25-mm. tube, whence $[\alpha]_D^{17} - 50.75^\circ$. The *dl*-ester boiled at $228\text{--}231^\circ/48$ mm., and had $d_4^{17} 0.9757$.

Esters of the Tartaric Acids.—The rotatory powers of the esters of the tartaric acids with the methyl-*n*-hexylcarbinols have been determined in the hope that the results might be useful in supporting the conclusions of Patterson (Trans., 1907, 91, 705) as to the non-validity of van't Hoff's theory of optical superposition. The rotatory powers observed were not in accordance with this theory, but owing to the failure of all attempts to prepare the corresponding esters of *i*-tartaric acid these results do not give a strict proof of its non-validity, such as Patterson has furnished in his work on the menthyl tartrates. McCrae has described ethyl β -octyl *d*-tartrate (Trans., 1901, 79, 1103) and di- β -octyl *d*-tartrate (Trans., 1902, 81, 1221) as viscous oils with a rancid odour, and the latter as having a yellow colour. The esters mentioned

in table X have all been obtained as highly-refracting, colourless liquids, somewhat viscous and practically odourless. The preparation of the di- β -octyl tartrates is readily carried out as follows: 40 grams of the required methyl-*n*-hexylcarbinol and 10 grams of the diethyl ester of the tartaric acid are mixed and saturated at a temperature below 0° with hydrogen chloride. After some days, the hydrogen chloride and about 5 c.c. of the mixture are distilled off under diminished pressure on a water-bath. The main bulk of the mixture is then again saturated with hydrogen chloride as before, and kept for a week. The excess of alcohol, along with the hydrogen chloride, is now removed by distillation under a pressure of about 20 mm., and the ester carefully fractionated under a pressure of about 6 mm. One distillation is generally sufficient to give a product of constant rotation, the neutral esters boiling between 202° and 210°/6 mm.

In view of the discrepancy between McCrae's results and those here recorded, specimens of di- β -octyl *d*-tartrate were prepared from Kahlbaum's alcohol (with a slight levorotation) and both diethyl and dimethyl *d*-tartrate, each preparation being found to have $[\alpha]_D^{17} + 10.99^\circ$, whereas McCrae's value is $[\alpha]_D^{18} + 7.06^\circ$. Similar preparations from the pure *dl*-alcohol and diethyl and dimethyl *d*-tartrates had $[\alpha]_D^{17} + 11.18^\circ$ and $+ 11.02^\circ$ respectively. In the preparation of these esters from Kahlbaum's alcohol it was found that the rotation of the unesterified alcohol varied slightly from that of the original sample. As purchased, it had, in a 2-dm. tube, $\alpha - 0.14^\circ$ to $- 0.17^\circ$, whilst the unesterified alcohol had $\alpha - 0.05^\circ$ to $- 0.07^\circ$. In the course of the lengthy series of experiments summarised on p. 48, ethyl *dl*- β -octyl *d*-tartrate was isolated. It boils at 187—190°/7 mm., has $d_4^{17} 1.0568$, and $[\alpha]_D^{17} + 8.55^\circ$, a value higher than that recorded by McCrae (*loc. cit.*), who gives $[\alpha]_D^{16} + 7.63^\circ$.

Attempts to prepare the pure β -octyl esters of *i*-tartaric acid were failures, these compounds apparently decomposing before distillation.*

TABLE X.

*The Di- β -Octyl Esters of the Tartaric Acids.**Specific Rotatory Powers and Densities.*

		<i>d</i> -Tartaric acid.	<i>l</i> -Tartaric acid.	<i>r</i> -Tartaric acid.
<i>d</i> -Methyl- <i>n</i> -hexylcarbinol,	$[\alpha]_D^{17} \dots$	+ 24.06	+ 2.06	+ 14.12
	$d_4^{17} \dots\dots$	1.0165	1.0081	1.0047
<i>l</i> -Methyl- <i>n</i> -hexylcarbinol,	$[\alpha]_D^{17} \dots$	- 1.93	- 24.20	- 14.03
	$d_4^{17} \dots\dots$	1.0171	1.0059	1.0058
<i>dl</i> -Methyl- <i>n</i> -hexylcarbinol,	$[\alpha]_D^{17} \dots$	+ 11.02	- 11.00	—
	$d_4^{17} \dots\dots$	1.0148	1.0069	—

* The authors are greatly indebted to Dr. M. O. Forster, F.R.S., who attempted to distil a sample of one of these esters. He found that violent decomposition set in at about 160° when the pressure was only 0.5 mm.

Halides Corresponding with the Methyl-n-hexylcarbinols.

d- and *l*-Methyl-*n*-hexylcarbinols react fairly readily with hydrogen iodide, bromide or chloride, the formation of the halide being accompanied by a change in the sign of the rotation. The β -iodo-octanes are obtained when the alcohols are saturated at 0° with hydrogen iodide and kept for about five hours. In the case of the bromides and chlorides, the mixtures similarly prepared are heated at 100° in sealed tubes for one hour.

These halides are partly racemised if the reactions are not carried out under the above conditions, higher temperatures or prolonged heating always resulting in the products formed being of lower rotatory power. All the preparations obtained were unaltered in rotatory power after prolonged shaking with cold concentrated sulphuric acid. These active halides do not appear to undergo autoracemisation, as a specimen of *l*- β -bromo-octane was found to be unaltered in rotatory power two and a-half years after its preparation.

Various constants for these halides are given in table XI; the following additional ones were determined for *l*- β -bromo-octane: $d_4^{13.8}$ 1.0927, d_4^{26} 1.0805, d_4^{37} 1.0688, and d_4^{53} 1.0532; $[\alpha]_D$ -31.07° at 4°, -30.33° at 13.1°, -29.05° at 30°, -28.62° at 37.4°, -27.81° at 50°, -26.56° at 69°, and -25.18° at 92°.

TABLE XI.

Halides from Methyl-n-hexylcarbinol.

	Boiling point.	d_4^{17} .	α^{17} in 50-mm. tube.	α^{17} D.
<i>d</i> - β -Iodo-octane	101°/22 mm.	1.3314	+26.51°	+39.83°
<i>l</i> - β -Iodo-octane	92°/12 "	1.3299	-26.97	-40.56
<i>d</i> - β -Bromo-octane ...	74°/18 "	1.0895	+14.98	+27.53
<i>l</i> - β -Bromo-octane ...	71°/14 "	1.0914	-14.99	-27.47
<i>d</i> - β -Chloro-octane ...	75°/28 "	0.8658	+8.83	+20.40
<i>l</i> - β -Chloro-octane ...	70°/25 "	0.8628	-8.82	-20.44

Several experiments were carried out in which the halides were treated under varying conditions with potassium acetate. Although in every case the resulting β -octyl acetate had a rotation opposite in sign to the halide used, yet it was never obtained optically pure, some racemisation invariably taking place during the formation of the acetate, whilst possibly the halides themselves were not optically pure.

d-Methyl-n-heptyl-, d-Methyl-n-octyl-, and d-Methyl-n-nonyl-carbinols.

These were each prepared in two ways, namely, from the brucine and from the strychnine salts of the dextrorotatory hydrogen phthalic esters. The following constants were determined:

d-Methyl-n-heptylcarbinol boiled at 105°/19 mm., had $d_4^{18.1}$ 0.8281, d_4^{25} 0.8202, $d_4^{34.2}$ 0.8129, $d_4^{45.5}$ 0.8043, d_4^{76} 0.7799, and $[\alpha]_D$ +8.98° at 19°, +8.88° at 26.5°, +8.71° at 34°, +8.55° at 49.5°, +8.44° at 66°, and +8.39° at 72°.

d-Methyl-n-octylcarbinol boiled at 110—111°/11 mm., had $d_4^{14.3}$ 0.8293, $d_4^{24.5}$ 0.8220, $d_4^{42.2}$ 0.8096, d_4^{61} 0.7935, and d_4^{146} 0.7222, and $[\alpha]_D$ +8.74° at 17°, +8.55° at 26.4°, +8.37° at 35.4°, +8.02° at 58.9°, +7.75° at 93°, and +7.81° at 146°.

d-Methyl-n-nonylcarbinol boiled at 128°/20 mm. and solidified when cooled to a mass of stellate needles, which melted at 12°. It had d_4^{14} 0.8318, $d_4^{27.1}$ 0.8226, $d_4^{37.5}$ 0.8145, $d_4^{54.9}$ 0.8017, $d_4^{72.5}$ 0.7896, and $[\alpha]_D$ +8.40° at 6°, +8.18° at 18°, +8.03° at 25.7°, +7.88° at 35°, +7.67° at 48.7°, +7.55° at 59°, +7.34° at 73°, and +7.27° at 92°.

d-Methyl-n-decylcarbinol, obtained from the brucine salt of the dextrorotatory hydrogen phthalic ester, boiled at 146°/24 mm., and, when cooled, set to a mass of stout, prismatic rods in a crystalline matrix. This melted at 18.7°, had $d_4^{12.}$ 0.8369 (in a supercooled condition), $d_4^{27.4}$ 0.8265, $d_4^{38.9}$ 0.8182, $d_4^{51.2}$ 0.8090, $d_4^{60.6}$ 0.8016, and $[\alpha]_D$ +7.80° at 19°, +7.66° at 27°, +7.51° at 36.5°, +7.32° at 46.5°, +7.15° at 57.5°, +7.00° at 71°, and +6.88° at 93°.

d-Methyl-n-undecylcarbinol, obtained either from the brucine or strychnine salt of the dextrorotatory phthalic ester, boiled at 156—157°/17 mm., and set to a glistening, crystalline mass of prismatic needles, which melted at 30°. It had $d_4^{34.1}$ 0.8215, $d_4^{47.3}$ 0.8109, $d_4^{60.6}$ 0.8012, and $[\alpha]_D$ +7.10° at 25.5° (when supercooled), +6.98° at 33.5°, +6.74° at 48°, +6.55° at 56.5°, +6.42° at 71.9°, and +6.37° at 93°.

d-Methylisobutylcarbinol was obtained from the brucine salt of the dextrorotatory hydrogen phthalic ester and from the cinchonidine salt of dextrorotatory hydrogen succinic ester. It boiled at 65.5°/45 mm., had d_4^{19} 0.8083, d_4^{28} 0.8014, d_4^{50} 0.7824, $d_4^{75.5}$ 0.7596, and $[\alpha]_D$ +21.35° at 6.3°, +20.86° at 14°, +20.4° at 21.3°, +20.04° at 29.5°, +19.69° at 38.7°, +19.48° at 43°, +19.11° at 57°, +18.65° at 72°, and +18.25° at 94.3°.

l-Methylisobutylcarbinol, obtained from the brucine salt of the levorotatory hydrogen succinic ester, had $[\alpha]_D^{14}$ -20.80°.

d-Ethyl-n-hexylcarbinol, obtained from the brucine salt of the dextrorotatory hydrogen phthalic ester, boiled at 97°/17 mm., had $d_4^{16.8}$ 0.8281, $d_4^{26.3}$ 0.8202, $d_4^{37.9}$ 0.8129, $d_4^{54.4}$ 0.8043, $d_4^{78.5}$ 0.7799, and $[\alpha]_D$ +8.09° at 6.1°

+8.05° at 20.6°, +8.13° at 37.8°, +8.14° at 48.2°, and +8.2° as 70.5°.

l-Ethyl-*n*-hexylcarbinol, obtained from the cinchonidine salt of the lævorotatory hydrogen phthalic ester, boiled at 94°/13 mm., had d_4^{17} 0.8277, and $[\alpha]_D^{17}$ -7.96°.

Table XII shows some of the properties of the γ -chloro-, bromo-, and iodo-nonanes, which were prepared by the methods used in the case of the corresponding β -octane derivatives. In each case the alcohol yielded a halogen derivative with a rotatory power of opposite sign.

TABLE XII.

 γ -Halogen Derivatives of n-Nonane.

	Boiling point.	d_4^{17} .	$[\alpha]_D^{17}$.
<i>d</i> - γ -Chlorononane	87—89°/24 mm.	0.8588	+7.71°
<i>l</i> - γ -Chlorononane	101°/40 „	0.8540	-8.03
<i>d</i> - γ -Bromononane	112°/32 „	1.0900	+12.90
<i>l</i> - γ -Bromononane	96—97°/22 „	1.0897	-13.39
<i>d</i> - γ -Iodononane	120°/27 „	1.2940	+17.65
<i>l</i> - γ -Iodononane	122°/37 „	1.2873	-17.50

d-Phenylmethylcarbinol, $C_6H_5 \cdot CH(OH) \cdot CH_3$, obtained from the brucine salt of the dextro-rotatory hydrogen succinic ester, boiled at 100°/18 mm., had $d_4^{13.3}$ 1.0191, $d_4^{26.2}$ 1.0079, $d_4^{35.2}$ 1.0019, d_4^{48} 0.9911, $d_4^{55.4}$ 0.9846, $d_4^{80.2}$ 0.9646, and $[\alpha]_D$ +42.90° at 6°, +42.85° at 27°, +42.74° at 36.8°, +42.69° at 47°, +42.53° at 58°, +42.27° at 71°, and +41.33° at 94°.

d-Phenylethylcarbinol, obtained from the brucine salt of the dextro-rotatory hydrogen succinic ester, boiled at 115—116°/25 mm., had d_4^{17} 0.9962, and $[\alpha]_D^{17}$ +27.35°.

l-Phenylethylcarbinol, obtained from the cinchonidine salt of the corresponding lævorotatory ester, boiled at 115—116°/25 mm., had $d_4^{13.8}$ 0.9982, $d_4^{28.8}$ 0.9872, $d_4^{42.7}$ 0.9755, $d_4^{60.5}$ 0.9538, and $[\alpha]_D$ -24.76° at 5.3°, -26.83° at 15.2°, -29.07° at 27.2°, -30.34° at 35°, -33.90° at 64.5°, and -35.58° at 94°.

The corresponding chloro-compounds were obtained when these three alcohols were saturated at 0° with hydrogen chloride and kept for some hours.

l- α -Chloroethylbenzene, $C_6H_5 \cdot CHCl \cdot CH_3$, from the dextro-rotatory carbinol, boiled at 86°/22 mm., had d_4^{17} 1.0642, and $[\alpha]_D^{17}$ -5.80°.

The lævorotatory phenylethylcarbinol yielded *d*- α -chloropropylbenzene, which boiled at 86—87°/15 mm., had d_4^{17} 1.0429, and $[\alpha]_D^{17}$ +3.79°. The corresponding dextro-rotatory chloro-compound boiled at 95°/25 mm., and had d_4^{17} 1.0430 and $[\alpha]_D^{17}$ -3.87°.

The authors have much pleasure in acknowledging the assistance given to them by Miss Annie Higson, B.Sc. (Lond.), who prepared and

carried out many experiments with methylethylcarbinol, and by Mr. G. T. Byrne, B.Sc. (Manc.), who has repeated several of the resolutions described.

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VIII.—*The Chemistry of Mesothorium.**

By FREDERICK SODDY, M.A., F.R.S.

MESOTHORIUM, the first product of the thorium disintegration series, and the parent of radiothorium, was discovered three years ago by O. Hahn (*Ber.*, 1907, **40**, 1462). Although for the past few months powerfully radioactive preparations of this substance, prepared by Hahn during the course of the manufacture of thorium salts from monazite sand in the works of Dr. Knöfler & Co., Plotzensee, Berlin, have been put on the market, nothing has been allowed to transpire concerning the chemical processes by which the separation is effected. Rutherford, in a Royal Institution Lecture (January 31st, 1908), drew attention to the value of mesothorium as a possible substitute for radium in many experiments, owing to the large scale on which thorium compounds are commercially manufactured. Although mesothorium is not a permanent source of radioactivity, like radium practically is, yet the period of average life, about eight years, is sufficiently long to make it a very useful substance if it could be prepared on a large scale. At the beginning of the present year, powerful sources of thorium radioactivity were needed for certain experiments, and as at that time there seemed no possibility of obtaining it in any other way, experiments were undertaken on the separation of mesothorium from thorium minerals, commencing with thorianite.

The discovery of radiothorium by Sir William Ramsay and O. Hahn, which preceded that of mesothorium, was made in the course of the treatment of a large quantity of thorianite for radium. The material was fused with potassium hydrogen sulphate, the insoluble residue being treated in the same way as the radium-

* Since this paper was written there has appeared a communication on the same subject by W. Marckwald (*Ber.*, 1910, **43**, 3420) which anticipates the discovery of the chemical identity of mesothorium-1 and radium.

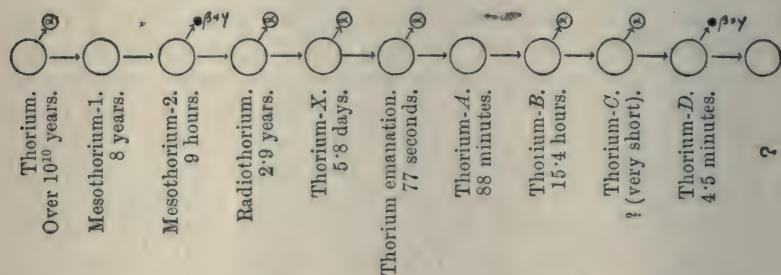
containing residues from pitchblende, to extract the barium as chloride. Radiothorium was discovered in this product (Sir W. Ramsay, *J. Chim. Phys.*, 1905, **3**, 617; O. Hahn, *Jahrb. Radioactiv. Elektronik.*, 1905, **2**, 234). Subsequently a study of the chemical properties of radiothorium by Elster and Geitel (*Physikal. Zeitsch.*, 1906, **7**, 445) and G. A. Blanc (*Phil. Mag.*, 1905, [vi], **9**, 148), and the work of Boltwood (*Amer. J. Sci.*, 1907, [iv], **25**, 93), resulted in the view at present held, that radiothorium resembles thorium completely and cannot be separated from it by chemical processes, and that the radiothorium prepared by Hahn was due to the separation of mesothorium and the spontaneous production of radiothorium from it with the lapse of time. What little is known of the chemistry of mesothorium we owe to Boltwood, who showed that the original process employed in the separation of thorium-X (Rutherford and Soddy, *Trans.*, 1902, **81**, 343, 837) in the filtrate after precipitation of thorium by ammonia, separated also the mesothorium. He also precipitated barium sulphate in a dilute solution of a thorium salt, thinking that the adsorption of radiothorium by the barium sulphate might explain Hahn's results with thorianite. He found, however, that mesothorium, but not radiothorium, was separated with the barium sulphate, and concludes: "It appears quite likely therefore that the entraining action of barium sulphate on mesothorium was directly responsible for the presence of radiothorium in the thorianite residues [of Hahn]." Since Sir W. Ramsay and Hahn were dealing with a mixture of radiothorium and mesothorium in genetic relationship, nothing can be learnt from the original papers on radiothorium (*loc. cit.*) of the chemistry of mesothorium,* as it is uncertain throughout to which substance the reactions apply, whilst in Hahn's later papers on mesothorium (*loc. cit.*, and *Physikal. Zeitsch.*, 1907, **8**, 277) no information on this subject is given.

Thorianite is, from the radioactive point of view, the most complex material it is possible to work with, as it contains every one of the thirty or more radioactive elements known, in important quantity, the penetrating radiation contributed by the uranium and thorium series being, for the specimen of thorianite examined (which contained about three times as much thorium as uranium), of very similar intensity. The thorium disintegration series, as at present known, is shown below to facilitate reference, and no phenomena were encountered in the course of the work which could

* Thus Sir W. Ramsay, for example, in his paper "Radio-thorium" (*J. Chim. Phys.*, 1905, **3**, 623) says, "Le nouveau corps se précipite partiellement avec le radium, en ajoutant aux sels de thorium d'abord un sel de baryum et ensuite de l'acide sulfurique; et l'on peut effectuer sa séparation du radium par un des procédés dont nous avons donné la description."

not readily be explained by this succession of changes and by the known changes in the radium series.

Throughout, γ -ray methods of measurement with lead electroscopes (Soddy and Russell, *Phil. Mag.*, 1910, [vi], **19**, 752) have been employed whenever possible, as by these means the difficulty of comparing together specimens differing greatly in density and weight is avoided. The only objection to it is that considerable amounts of material must be employed to produce effects sufficiently large to measure with accuracy. In dealing with monazite, a special very large lead cylindrical electroscope (22 cm. high and 22 cm. diameter) was constructed so as to give greater sensitiveness. The lead used, which was 3 to 4 mm. thick, was taken from the roof of a very old building, in which any radio-lead initially present would have decayed (*Ann. Reports*, 1906, **3**, 365), so that the natural leak might be as small as possible. It proved very successful. A very



complete study of the γ -radiation of the various radio-elements, in conjunction with Mr. Russell, has recently been concluded, and the section dealing with the γ -rays of thorium has appeared in the *Philosophical Magazine* (1911, [vi], **21**, 130). It suffices to state here that the two thorium types of γ -rays, from mesothorium-2 and thorium-D, both in penetrating power and in the ratio of their intensity to that of the accompanying β -rays, are extremely similar to the radium type of γ -rays which are given by radium-C. Radium-C, mesothorium-2, and thorium-D, alone of all the known radioactive constituents, give γ -radiation of sufficient intensity to affect the measurements. When β -ray methods are employed, the possible effects due to uranium-X, radium-E, and, perhaps, actinium-C must also be remembered, but the γ -rays from these substances are negligible. In all measurements of γ -rays, the preparations were contained in sealed test-tubes, so as to retain the radium emanation completely. In spite of the complexity of thorianite, no difficulty was ever experienced in deducing from the variations of the γ -activity with time the radioactive constituents present and their relative amount, although two of the periods

(those of the radium emanation and thorium-*X*) controlling the γ -ray variations are identical.

For the specimen of thorianite worked with, moreover, the γ -activity contributed by thorium-*D* was very similar in intensity to that contributed by radium-*C*, so that, frequently, preparations appeared to remain of constant activity for long periods, when what was really taking place was a simultaneous complete decay of thorium-*X* (and in consequence thorium-*D*) and a concomitant reproduction of radium emanation (and in consequence radium-*C*) from the radium. The analysis of the effects was no doubt enormously simplified, because, as will appear in the sequel, mesothorium-1, radium, and thorium-*X* appear to form a trio of chemically non-separable elements.

Experiments were started with a solution of thorianite in nitric acid by the two known methods, capable of separating mesothorium, due to Boltwood. The repeated precipitation of the solution with ammonia and evaporation and ignition of the filtrate, as in the preparation of thorium-*X*, effects a complete separation in sufficiently dilute solution, but in an attempt to apply it to considerable quantities with more concentrated solutions, the separation was partial, and the fraction separated varied capriciously. The precipitation in the thorianite solution of barium as sulphate, although at first not very successful, was found ultimately, under proper conditions, to yield good results, even in concentrated solutions the separation being nearly complete. In one experiment 26 grams of barium nitrate was dissolved in a solution of 600 grams of thorianite in nitric acid, from which most of the excess of acid had been evaporated. The solution, of volume about 1.5 litres, was put in a Winchester quart bottle, excess of dilute sulphuric acid added, and the bottle shaken for an hour on a shaking machine. The separation of the mesothorium was practically complete, a second precipitation yielding a precipitate possessing an activity not greater than could be accounted for by the regeneration of thorium-*X* in the time between the precipitations.

About 5 kilograms of thorianite were treated by this method, and the γ -activity of the products, sealed up in test-tubes, was kept under observation for some time. The first precipitate from the solution increased rapidly in γ -activity by about 50 per cent. in the course of two days, and then remained nearly constant. During filtering and drying, mesothorium-2 is usually produced in nearly equilibrium amount before the first measurement. The increase for the first two days is due to the formation of thorium-*D* from thorium-*X*. After that time the decay of thorium-*X* just balanced the production of radium-*C* from the radium as already explained,

so that the activity remains sensibly constant. For the subsequent precipitates the γ -activity was due mainly to thorium-*X*, regenerated between the precipitations, and, after reaching the maximum, steadily decayed.

In this way, from the 5 kilograms of thorianite a total weight of about 200 grams of barium sulphates of various activities was separated. Up to this time it was considered, as Boltwood had supposed, that the mesothorium was merely adsorbed by the barium sulphate. Uranium-*X* was, in a recent research (F. Soddy and A. S. Russell, *Phil. Mag.*, 1909, [vi], **18**, 620), frequently separated by adsorption with barium sulphate, and was found to be readily separable from the barium after solution of the barium sulphate, by precipitating with ammonia in presence of a trace of iron.

In the hope of being able to effect a preliminary concentration of the mesothorium from the barium, to a portion of one of the sulphate precipitates, after conversion into chloride, a small quantity of dilute sulphuric acid was added to precipitate a small fraction of the barium as sulphate. The precipitate so obtained, however, was no more and no less active than the same weight of original material. Other attempts to concentrate the mesothorium from the barium, chemically, failed, and the conclusion was drawn that the separation of mesothorium with barium is due, not to an adsorption by the barium sulphate, as had previously been assumed, but to a chemical resemblance between the two elements.

The whole of the active barium sulphate was converted into chloride by ignition with sugar-carbon in separate small quantities in quartz crucibles, and the barium sulphide dissolved in hydrochloric acid. The crude chlorides in acid solution were freed from lead by hydrogen sulphide, made alkaline with ammonia, and filtered from the small iron and thorium hydroxide precipitate. A fractional crystallisation of the barium chloride was then commenced to concentrate the radium present from the barium. The various precipitates had been sorted into three grades, according to their activity, and worked up into pure chlorides separately. The raw material for the fractionations thus comprised three preparations of weights 52, 69, and 105 grams, and relative activities roughly as 5:2:1. As it was then unknown whether the separation of the barium from the mesothorium would be possible, the fractions were not mixed, but dissolved separately. Fractionation was carried out for separating radium from barium in the usual way, the mother liquor of the richer fraction being used to dissolve the crystals of the next richest. Preliminary tests showed that the process was very effective in concentrating the mesothorium as well as the radium from the barium. In a few days three fractions were

again made up, of weights 57, 97·5, and 76·5 grams. Mesothorium-2 was separated from each separately by adding 10 milligrams of thorium nitrate, and precipitating with ammonia. The relative activities of these mesothorium-2 precipitates were as 25·3 : 4·3 : 1. The mesothorium in equal weights of barium chloride was therefore as 34 : 3·4 : 1. This showed that the mesothorium had been effectively concentrated by the fractional crystallisation, the crystals being enriched, and the mother liquor impoverished, as in the case of radium. The three fractions were dissolved, left for a week, then evaporated to dryness and sealed up in test-tubes, and the γ -activity measured over a period of six weeks, 10 grams only of the first fraction being taken for the test. The ratio between the initial and subsequently generated activity gives the relative proportions of mesothorium and radium. These ratios were in order of richness of the preparation, 0·52, 0·46, and 0·56. Hence mesothorium follows the radium extremely closely in the fractionations. The small differences in the ratio, since the raw material of the fractionations was not homogeneous, but derived from different quantities of thorianite, are not greater than might be accounted for by variations in the composition of the mineral, or by the presence, possibly, of thorium-X from regenerated radiothorium. The measurements were only rough, whereas those which follow were done with the greatest possible accuracy.

In order to settle whether any alteration at all in the proportion of the mesothorium and radium was produced by fractional crystallisation, the most active fraction, all but the 10 gram sample sealed up for the previous tests, was refractionated as before. The richest fractions, withdrawn from the process after the fifth and eighth successive fractionations, were combined and labelled *AA*. A part of the 10 gram sample of the original material was taken, and labelled *A*. The two specimens were dissolved in water at the same time, freed from mesothorium-2 by precipitation of thorium hydroxide in the solution as before, evaporated, and sealed up. *A* weighed 2·38 grams, and *AA* 2·09 grams. The γ -rays were compared after two days, when mesothorium-2 is again in equilibrium, and at intervals subsequently. The measurements give the means of telling exactly whether any alteration in the ratio of the radium and mesothorium has been effected by the further fractionation.

Fraction *AA* proved to be 8·75 times as active as fraction *A*, showing that a concentration of the active material in the ratio 10 : 1 had been effected. Nevertheless, the proportions of radium and mesothorium in the two preparations were identical. The ratio of the activities remained unchanged within the error of

measurement, which may be estimated at less than 2 per cent., over the period from the first day after preparation onward, during which the activity more than doubled, owing to the accumulation of the radium emanation. In order the more accurately to compare the two preparations, measurements were taken not only of the two in the same position beneath the electroscope, but also of the stronger preparation at a greater distance, so that the effects compared should be of the same order. The following table shows the actual readings of the electroscope in divisions per minute, corrected for the natural leak (about 4.8), and the ratio between them for the two positions.

Day.	Fraction <i>A</i> .	Fraction <i>AA</i> .		Ratios.	
1st.....	10.5	91.5	12.05	8.7	1.14
2nd	13.1	115.0	14.95	8.8	1.14
3rd	15.0	133.0	17.35	8.85	1.15
7th	19.65	170.8	22.3	8.7	1.13
13th	23.9	203.0	26.6	8.5	1.12
34th	26.0	224.0	29.5	8.6	1.14

The fractionation process, from which the fraction *AA* was derived, was continued until twenty-four sets of fractionations had been performed. The products were then combined in two final fractions, the one, labelled *C*, consisting of the weak, and the other, labelled *B*, of the rich fractions. Thus the most active fraction of the original material was obtained in three fractions, *AA*, *B*, and *C*, the weights of which were 2.09, 2.27, and 38 grams respectively, and the relative activities as 4.6 : 3.85 : 1. The concentrations of the radioactive matter in the three fractions were therefore as 84 : 64 : 1. Fractions *B* and *C* were kept dissolved in water for some days, so that mesothorium-2 should be initially in equilibrium, then evaporated to dryness, sealed up in test-tubes, measured immediately, and again after twenty-one days. The relative activity of the two fractions was exactly the same in the two tests, showing that the fractionation process which had altered the concentration of the radioactive matter sixty-two times had not affected the ratio of the two radioactive constituents. For each fraction the proportion of the activity contributed by the mesothorium was almost exactly one-half that contributed by the radium, which is practically the same as that found initially.

This experiment proves conclusively therefore that in the fractional crystallisation of barium chloride, containing mesothorium and radium, the mesothorium and radium behave as a single substance, and there is no hope of separating them by this method. With the knowledge gained of the chemical nature of mesothorium, a good many further experiments were done on its

separation from thorianite, which need not be detailed. They all bore out the view that mesothorium and barium are chemically analogous. It was found that a practically complete separation of the mesothorium and radium from thorium in the thorianite solution could most favourably be effected by adding a small quantity of barium nitrate and a considerable quantity of strong nitric acid, and precipitating the thorium with oxalic acid in the strongly acid solution. The mesothorium is precipitated from the filtrate by pouring it into excess of sodium carbonate solution (which keeps the uranium dissolved), and recovered from the solution of the precipitate in nitric acid by precipitating the barium with sulphuric acid.

In the first experiment with monazite sand, 400 grams were dissolved, by heating it with twice its weight of sulphuric acid and stirring the product with cold water, exactly as in the technical working up of the material. The muddy liquor obtained was decanted from the unattacked sand, which constituted about 20 per cent. of the whole, and left to deposit its sediment. This weighed 4.8 grams, and consisted largely of calcium sulphate. It was labelled *A*. One gram of barium nitrate was dissolved, and added slowly to the clear monazite solution, with efficient stirring. The precipitate (labelled *B*) weighed 1.8 grams. Tested by γ -ray methods, the undissolved sand retained about 4.5 per cent. of the total activity of the material. The β -activities of the sediment *A* and precipitate *B* were as 1 to 3 initially, and as 1 to 2 after forty days. Thus, under the ordinary conditions of the thorium manufacture, an important part of the mesothorium is lost in the insoluble sediments. The chemical behaviour of mesothorium, as is to be expected, is indefinite in the absence of sufficient barium to be quantitatively separable. Monazite contains much less uranium and therefore radium, relatively to thorium, than thorianite, and the γ -rays of the preparation *B* in consequence fell to about half its maximum value in the course of a month, owing to the effect of the decay of thorium-*X* exceeding the growth of radium-*C*.

Further experiments with 400 and 800 grams of monazite sand were made as before, except that about 0.1 per cent. of barium carbonate was mixed with the sand before heating. The sediment obtained from the muddy solution now contained practically all the mesothorium and radium in the monazite. One such sediment, from 800 grams of monazite sand, weighed 14.5 grams and contained practically the whole of the mesothorium in the material. Its γ -ray activity at the maximum, three days after preparation, was about 70 per cent. of that of the original material. The unattacked sand retained 8 per cent. A further precipitate of 1.6 grams of

barium sulphate formed in the clear monazite solution possessed a small initial activity, due to regenerated thorium-*X* only, which almost completely decayed in the course of a month. Certainly less than 5 per cent. of the mesothorium in the sediment was present. As throughout the work thorium-*X*, mesothorium, and radium have always been separated together, the presence of thorium-*X* and absence of mesothorium in this precipitate may be regarded as clear evidence that practically the whole of the mesothorium can be separated from monazite by the method described. The γ -radiation of the main sediment fell to about 57 per cent. of its maximum value after a month, as the effect of the decay of thorium-*X* overpowers the increase due to the generation of radium-*C*.

In the course of two or three years it is to be expected that the preparation will rise in activity to somewhat more than its initial value, due to the regeneration of radiothorium, and in consequence thorium-*X* (and also of radium-*C*, which does not contribute to the initial activity). Then it will decay exponentially, with the period of mesothorium-1, to the constant small proportion contributed by the radium.

A part of this sediment was boiled with sodium carbonate, washed free from sulphates, and dissolved in hydrochloric acid. It left an inactive residue, mainly silica, whilst from the solution practically the whole of the radioactive matter was precipitated with the barium chloride by saturating it with hydrogen chloride. This is further evidence of the resemblance between mesothorium and radium. All the methods effective in the concentration of the latter which were tried serve equally well for mesothorium.

In going over all the measurements, which refer to more than thirty preparations, the activity of which was kept under observation for a month or longer, there is clear evidence also that thorium-*X* is always separated in any chemical operation in the same proportion as mesothorium and radium. It appears that the behaviour observed by Boltwood for the one reaction, precipitation with ammonia, is general. Certain apparent exceptions shown in the preparations measured were found, on referring back to the details of the separation, to be due to a lapse of time after the thorium-*X* had been separated from the mineral before the first measurement. In these circumstances, owing to the decay of the thorium-*X* after separation, its proportionate activity compared with that of mesothorium and radium appears low. Although no separate examination of the point has been made, there is good reason to believe that mesothorium, radium, and thorium-*X* are a chemically inseparable trio. It should be mentioned, however, that

G. Hoffmann (*Physikal. Zeitsch.*, 1907, **8**, 553), from a comparison of the coefficient of diffusion and ionic mobility of thorium-*X* in solution, deduced from Nernst's theory that the thorium-*X* ion is singly charged, and is therefore univalent. The conditions under which the radioactive measurements were carried out, however, were very far from definite. In the more recent work of Strömholm and Svedberg (*Zeitsch. anorg. Chem.*, 1909, **61**, 338; **63**, 197), some important additions have been made to the chemistry of the radio-elements. The method employed was new and ingenious. By crystallising various salts in solutions containing radioactive constituents, they sought to determine to which of the known elements the radio-elements were isomorphous. They concluded that no differences existed, even from the quantitative point of view, between thorium-*X*, actinium-*X*, and radium. So far as thorium-*X* is concerned, this agrees perfectly with the results given in this paper. They point out that in the thorium, actinium, and uranium-radium series the three emanations are identical chemically, being members of the family of inert gases. The preceding members, thorium-*X*, actinium-*X*, and radium, are again identical, all being members of the alkaline earth family. Next to these come radiothorium, radioactinium, and ionium, which are all similar, but they are inclined to put in the Periodic Table the respective groups ionium, uranium-*X*, radio-uranium; radioactinium, actinium; and radiothorium, mesothorium, thorium, as analogous to the rare-earth group lanthanum to ytterbium, as follows:

	0.	1.	2.	3-4.	
5th Period	Xe	Cs	Ba	La - Yb	
6th Period	<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 3em; vertical-align: middle;">{</div> <div style="display: inline-block; vertical-align: middle;"> RaEm AcEm ThEm </div> </div>	<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 3em; vertical-align: middle;">—</div> </div>	<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 3em; vertical-align: middle;">{</div> <div style="display: inline-block; vertical-align: middle;"> Ra AcX ThX </div> </div>	<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 3em; vertical-align: middle;">}</div> <div style="display: inline-block; vertical-align: middle;"> Ionium (UX, RaU) RaAc, Ac RaTh, MsTh, Th </div> </div>	}

Their work on mesothorium is indefinite and in disagreement, for the most part, with the results in this paper, that mesothorium-1 is identical chemically with radium and thorium-*X*. For example they state that ammonia precipitates all elements of the thorium series except thorium-*X*, and that mesothorium is not precipitated, like radium, along with barium sulphate, citing in support of this last some experiments, which, in their second paper, they withdraw because they have not been able to repeat them. It is clear that the chemical identity of mesothorium with radium completely negatives the above attempt to bring the radio-elements into the Periodic Table. The elements radiothorium, mesothorium, thorium suggest anything rather than the rare-earth group lanthanum to ytterbium.

It appears that chemistry has to consider cases, in direct

opposition to the principle of the Periodic Law, of complete chemical identity between elements presumably of different atomic weight, and no doubt some profound general law underlies these new relationships. Apart from the case of the three emanations, for which chemical identity is necessarily a common property of the whole group, we have, in addition to the case of radiolead (210·4) and lead (207·1), which are chemically inseparable, two well-defined groups of triplets: (1) Thorium (232·4), Ionium (230·5), Radiothorium (228·4); (2) Mesothorium-1 (228·4), Radium (226·4), Thorium-X (224·4), in which the chemical similarity is apparently perfect. The atomic weights, estimated, for the unknown cases, by subtracting from the atomic weight of the parent substance the known number of helium atoms expelled in their formation, show a regular difference of two units between the successive members of these two groups. The first group consists of quadrivalent elements of the fourth vertical column and the second of bivalent elements of the second column of the Periodic System, and yet the atomic weight of the last member of the first, and first member of the second, group are, as far as is known, the same.

The chemical identity of the members of the above two groups is almost certainly much closer than anything previously known. In the rare-earth group, elements with neighbouring atomic weights are often so closely allied that they can only be separated after the most laborious fractionation, and distinguished by the difference in their equivalents. But as the latter are always very close, the test is a very rough one in comparison with what is possible for radio-elements. Take, for example, the case of ionium and thorium. Boltwood, Keetman, and, lastly, Auer von Welsbach have all failed completely to concentrate ionium from thorium, the latter after a most exhaustive examination, in which his unrivalled knowledge of the rare-earths was supplemented by the new, powerful methods of radioactive analysis (*Mitteilungen der Radium Kommission*, VI, *Sitzungsber. K. Akad. Wiss. Wien*, 1910, **119**, ii, a, 1). The question naturally arises whether some of the common elements may not, in reality, be mixtures of chemically non-separable elements in constant proportions, differing step-wise by whole units in atomic weight. This would certainly account for the lack of regular relationships between the numerical values of the atomic weights.

The examples given include all the known radio-elements with periods of average life longer than a year, except uranium,* whilst for this element the fact that it alone gives two α -particles per atom disintegrating, which probably are not derived from two

* Actinium can hardly be considered in this connexion as its chemistry is still relatively imperfectly known.

rapidly succeeding changes on account of the lowness of their range, is good ground for considering that uranium may also be a mixture of two chemically non-separable elements in constant proportion due to their genetic relationship, differing in atomic weight by four units. On this view, uranium may be analogous to thorium and radiothorium, except that there is no intermediate product of different chemical nature to reveal their separate identities.

It is natural that relationships such as these, even if they were general, should at first appear to be confined to the longer-lived radio-elements. For the shorter-lived substances, not only on account of the evanescent character of the material is it difficult to determine their true chemical nature. Adsorption plays a much larger part in the separation of the short-lived products than it does in the case of the longer-lived. The reason is not far to seek. Radioactivity is a function, not of mass, but of mass divided by the period of average life. Thus a given amount of an adsorbent may be able to adsorb similar amounts of two radioactive substances before becoming saturated. If, however, the one is much longer lived than the other, when quantities, not equal, but possessing similar radioactivity are acted on, the separation may be practically complete for the shorter-lived substance, and for the other practically inappreciable.* Polonium, although its period of average life is less than a year, has well-defined chemical properties, which have been elucidated by the exhaustive investigations of Mme. Curie and Marckwald. It will be interesting to see whether it does not prove to be identical with the still non-isolated "di-tellurium" of Mendeléeff, for the existence of which some recent evidence is forthcoming (W. R. Flint, *Amer. J. Sci.*, 1910, [iv], **30**, 209). It would at least be interesting to apply to the supposed mixtures of tellurium and di-tellurium the methods used by Marckwald in separating polonium from tellurium.

I desire to acknowledge the capable assistance of Mr. W. T. Munro in the preparation of the purified active barium chloride from thorianite.

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* This point of view also explains at once the remarkable observation of Ritzel (*Zeitsch. physikal. Chem.*, 1909, **67**, 725) that a trace of thorium sulphate completely prevents the adsorption of uranium-X by charcoal. For, according to Marckwald and Keetman, uranium-X is completely analogous chemically to thorium and cannot be separated from it.

IX.—Attempts to Prepare Glycerides of Amino-acids.

By ROMAN ALPERN and CHARLES WEIZMANN.

THE intention of the authors in commencing this work was to prepare glycerides of the simple amino-acids, for example, triaminotriacetin, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2)_2$, since in all probability substances of this nature would possess great physiological importance.

The direct combination of glycerol and glycine was found to be impossible, and while experiments in this direction were proceeding, Abderhalden (*Zeitsch. physiol. Chem.*, 1910, **65**, 53) published the results of experiments on the same lines, from which he drew the same conclusion.

The combination of α -halogen substituted acids with glycerol was then carried out, with the idea of subsequent displacement of the halogen by the amino-group.

EXPERIMENTAL.

Preparation of Trichlorotriacetin.

It was found that the preparation could be carried out conveniently in two ways:

(1) Direct condensation of chloroacetic acid and glycerol by means of zinc chloride:

Chloroacetic acid (3 mols.), freshly distilled, is dissolved in glycerol (1 mol.). To this mixture is added zinc chloride (3 mols.), and the whole is heated on the water-bath for five hours. Water is then added, the trichlorotriacetin extracted with ether, the ethereal solution washed with water, then with sodium carbonate solution, dried, and distilled. The yield is 60 per cent. of the theoretical.

Trichlorotriacetin is a colourless, viscid oil, with a bitter taste; it boils at $205\text{--}208^\circ/10$ mm.:

0.1098 gave 0.1334 CO_2 and 0.0376 H_2O . $\text{C} = 33.1$; $\text{H} = 3.8$.

0.1526 „ 0.2050 AgCl . $\text{Cl} = 33.0$.

$\text{C}_9\text{H}_{11}\text{O}_6\text{Cl}_3$ requires $\text{C} = 33.5$; $\text{H} = 3.4$; $\text{Cl} = 33.0$ per cent.

By condensing glycerol with bromoacetic acid in molecular quantities in an exactly similar manner, *α -monobromoacetin*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_2\text{Br}$, is obtained. This is a yellow oil, possessing a bitter taste, and boiling at $217\text{--}219^\circ/10$ mm.:

0.1555 gave 0.1670 CO_2 and 0.0560 H_2O . $\text{C} = 28.4$; $\text{H} = 4.0$.

$\text{C}_5\text{H}_9\text{O}_4\text{Br}$ requires $\text{C} = 28.1$; $\text{H} = 4.2$ per cent.

(2) By the action of dry hydrogen chloride on a mixture of glycerol and either chloroacetyl chloride or chloroacetic anhydride:

Dry hydrogen chloride is passed into a mixture of glycerol and either chloroacetyl chloride or chloroacetic anhydride until, in the first case, a homogeneous, viscous mass is obtained, and, in the second, two layers separate. Water is then added, and the trichlorotriacetin isolated as before.

This method is also applicable to the preparation of triacetin, a very good yield being obtained.

αα'-Dipropionin.

Propionic anhydride (2 mols.) and glycerol (1 mol.) are condensed as described above. A colourless, mobile liquid is obtained in 45 per cent. yield, which possesses an aromatic odour, but also recalls that of propionic acid. It boils at 170—173°/10 mm.:

0.1174 gave 0.2264 CO₂ and 0.0826 H₂O. C=52.6; H=7.8.

C₉H₁₆O₅ requires C=52.9; H=7.8 per cent.

The displacement of the halogen in trichlorotriacetin by the amino-group was not found possible under the conditions employed.

Dry gaseous ammonia, even at 0°, hydrolyses the ester with the production of glycol and chloroacetamide.

On boiling trichlorotriacetin in xylene solution with potassium phthalimide, reaction evidently took place. There was an abundant separation of potassium chloride, but from the viscous mass left by the evaporation of the xylene, nothing definite except phthalimide could be isolated.

αα'-Diacetoacetin, OH·CH(CH₂·O·CO·CH₂Ac)₂.

In the hope of obtaining β-amino-derivatives of the glycerides, αα'-diacetoacetin was prepared by condensing ethyl acetoacetate with glycerol by means of concentrated sulphuric acid.

To a mixture of glycerol (10 grams) and ethyl acetoacetate (30 grams), 40 to 50 drops of concentrated sulphuric acid are added very slowly with constant shaking. After ten minutes, the two layers should have disappeared, and warming gently to about 50° facilitates this. If the layers do not now mix, a few more drops of sulphuric acid are added. The mixture is then kept for twelve hours; after it has been extracted with ether, the yellow ethereal solution is washed with a little water, dried, and distilled:

0.0926 gave 0.1762 CO₂ and 0.0666 H₂O. C=51.7; H=7.9.

C₁₁H₁₆O₇ requires C=52.9; H=7.8 per cent.

αα'-Diacetoacetin is a viscid, yellow oil, boiling at 157—160°/14 mm., with an odour resembling that of ethyl acetoacetate. It is

insoluble in sodium carbonate solution, and gives a reddish-brown coloration with ferric chloride.

An attempt was then made to condense $\alpha\alpha'$ -diacetoacetin with ethyl glycine (compare Fischer, *Ber.*, 1901, **34**, 433).

A very small quantity of a substance was obtained, which was neither the product of condensation of $\alpha\alpha'$ -diacetoacetin and ethyl glycine nor diketopiperazine, but the amount was too small to permit of further investigation.

$\alpha\beta$ -Dichloro- α' -acetoacetin, $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$.

If, instead of concentrated sulphuric acid, a stream of dry hydrogen chloride is used as a condensing agent, $\alpha\beta$ -dichlorohydrin condenses with ethyl acetoacetate to form $\alpha\beta$ -dichloro- α' -acetoacetin, which is a yellow oil, boiling at $103\text{--}105^\circ/14\text{ mm.}$:

0.1230 gave 0.1778 CO_2 and 0.0554 H_2O . $\text{C}=39.4$; $\text{H}=4.9$.

$\text{C}_7\text{H}_{10}\text{O}_3\text{Cl}_2$ requires $\text{C}=39.4$; $\text{H}=4.6$ per cent.

N-Allylglycine and its Ethyl Ester.

Attempts were also made to combine various derivatives of glycerol with ethyl glycine.

Epichlorohydrin, dichlorohydrin, and acrolein did not condense with ethyl glycine under all the conditions employed by the authors.

Allylamine, however, readily condenses with ethyl bromoacetate to form *ethyl N-allylglycine*, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$.

The condensation is carried out as follows. The calculated quantity of allylamine is added to ethyl bromoacetate in ethereal solution in small quantities at a time, the whole being cooled to 0° . At the end of an hour a 33 per cent. solution of sodium hydroxide is added, and then dry potassium carbonate until the aqueous layer acquires a syrupy consistency. This is extracted several times with ether, the ethereal solution dried, and distilled. The ester boils at $75\text{--}78^\circ/15\text{ mm.}$:

0.0586 gave 0.1248 CO_2 and 0.0498 H_2O . $\text{C}=58.1$; $\text{H}=9.4$.

0.1383 „ 11.5 c.c. N_2 at 19° and 756 mm. $\text{N}=9.5$.

0.1184 „ 10.1 c.c. N_2 „ 18° „ 756 mm. $\text{N}=9.8$.

$\text{C}_7\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C}=58.7$; $\text{H}=9.1$; $\text{N}=9.8$ per cent.

The best yield of the corresponding acid was obtained by hydrolysing the ester with methyl-alcoholic barium hydroxide. The barium is precipitated as sulphate, and the filtrate evaporated to dryness in a vacuum. The residue is extracted with water, and the solution evaporated to dryness in a vacuum. The product,

N-allylglycine, separates from methyl alcohol as a colourless, crystalline powder, melting at 158—159°:

0.1189 gave 12.8 c.c. N_2 at 15° and 752 mm. $N=12.47$.

$C_5H_9O_2N$ requires $N=12.17$ per cent.

In order to obtain a characteristic derivative of the acid, both the α - and β -naphthalenesulphonyl derivatives were prepared.

N- α -Naphthalenesulphonylallylglycine was prepared in the usual way. It is precipitated as an oil, which solidifies only after some days. It does not crystallise well from water.

N- β -Naphthalenesulphonylallylglycine was also prepared. It is precipitated as an oil, which solidifies in a short time. It crystallises from water in colourless, glistening plates, melting at 131—132°:

0.1320 gave 0.2841 CO_2 and 0.0585 H_2O . $C=58.7$; $H=4.92$.

$C_{15}H_{15}O_4NS$ requires $C=59.0$; $H=4.9$ per cent.

In conclusion, the authors wish to express their indebtedness to the Research Fund Committee of the Chemical Society for the grant which has enabled them to carry out this research.

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X.—Isomeric Chromous Chlorides.*

By WILLIAM ARTHUR KNIGHT and ELIZABETH MARY RICH.

PRUD'HOMME (*Bull. Soc. ind. Mulhouse*, 1889, **59**, 603) stated that chromous chloride was green in hot concentrated acid solution, although its cold dilute solution was blue; hence, from analogy to chromic salts, he assumed the existence of two isomeric forms in solution.

McBain (*Diss.*, Heidelberg) has confirmed this, and succeeded in isolating a solid dark green chromous chloride of unknown degree of hydration, which gave a green solution with water, the solution soon becoming azure-blue.

We have prepared pure chromous chloride by a greatly improved method, and, while confirming the existence of two isomeric chromous chlorides, have further discovered two new solid salts, which are merely lower hydrates of the blue isomeride, one being light green and the other pale blue.

The first part of the present paper deals with the conditions of

* This paper corresponds with the two abstracts in *Proceedings*, 1910, **26**, 47.

existence of all five hydrates and isomerides. It is shown that the blue isomeride in solution has the formula $\text{Cl}\cdot\text{Cr}\cdot\text{Cl}$, being highly dissociated into three ions, whilst the green isomeride, $\text{CrCl}\cdot\text{Cl}$, is well dissociated into two ions.

The Solid Modifications.

The blue hydrate, $\text{CrCl}_2\cdot 4\text{H}_2\text{O}$, was prepared by the following modification of Recoura's method* (*Ann. Chim. Phys.*, 1887, [vi], 10, 10). Chromous acetate is dissolved in concentrated hydrochloric acid in a vacuum,† and the clear solution is boiled down to dryness. If this distillation is too prolonged, or if it is interrupted overnight, the dark green isomeride is usually formed, whilst if the temperature rises above 51° after crystals have begun to appear, the product is pale blue or light green or white, but these are varieties of the blue isomeride, and are finally converted into the stable dark blue hydrate in presence of cold water. The blue crystals are washed by repeated decantation with pure acetone, and the final drying carried out with ether.

Crystals prepared in this way appear to undergo no alteration when left for many months, but, in spite of the high degree of purity of this chromous chloride (especially when it has been reprecipitated from saturated solution by concentrated hydrochloric acid), its solution, on exposure to the air, has a marked disagreeable odour.

The following solid chromous chlorides exist:

Dark blue crystals	$\text{CrCl}_2\cdot 4\text{H}_2\text{O}$
Dark green crystals	$\text{CrCl}_2\cdot 4\text{H}_2\text{O}$
Pale blue crystals	$\text{CrCl}_2\cdot 3\text{H}_2\text{O}$
Light green (amorphous?)	$\text{CrCl}_2\cdot 2\text{H}_2\text{O}$
White (amorphous?)	CrCl_2

Of these, the first and last were previously known. A direct analysis of the dark green variety was not made, since large quantities could be readily converted into the dry, dark blue modification in a closed flask, and vice versa; consequently, it was proved that the two isomerides are equally hydrated. The analyses of the remaining varieties were carried out by weighing a quantity of the

* Compare the other methods hitherto employed, which are difficult or laborious: Dammer, *Handb. d. anorg. Chem.*, Bd. III., 1893, 526; Koppel, *Zeitsch. anorg. Chem.*, 1905, 45, 359; Hittorf, *Zeitsch. physikal. Chem.*, 1898, 25, 729; 1899, 30, 481; Ostwald, *ibid.*, 1900, 35, 33, 204; Brauer, *ibid.*, 1901, 38, 441; Döring, *J. pr. Chem.*, 1902, [ii], 66, 65; 1906, [ii], 73, 392; Moissan, *Ann. Chim. Phys.*, 1882, [v], 25, 401; Loewel, *ibid.*, 40, 42; Mazzucchelli, *Gazzetta*, 1905, 35, i, 417; Böhringer & Söhne, D.R.-P. 115463.

† If all rubber connexions are well smeared with glycerol, a vacuum may be readily maintained for several months, if necessary.

dark blue crystalline modification in an evacuated flask of known weight, and then converting it into dry specimens of the various lower hydrates by distilling at constant temperature into an evacuated tube containing phosphoric oxide and weighing again. As a check, the lower hydrates in each case were reconverted into the dark blue crystals of the tetrahydrate, which were weighed once more. The transference in a vacuum of the crystals of the dark blue hydrate from one vessel to another was effected by shaking them through the connecting tubes, either with or without acetone.

Conclusive evidence was obtained that water, and not hydrogen chloride, was evolved from the hydrates, even on heating to 180° in a vacuum. This was established by direct analysis (both for chromium and chlorine) of the product obtained after one and the same specimen had been converted into all the modifications in succession.

The Pale Blue Crystalline Trihydrate, $\text{CrCl}_2 \cdot 3\text{H}_2\text{O}$.—This was prepared by distilling off water from the tetrahydrate at about 50° . This gives a mixture of pale blue trihydrate and light green dihydrate, $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$, but when water is added, the light green portion turns at once into the pale blue. The flask is then heated to 51° , and the pale blue modification which results is quickly dried at the ordinary temperature by evacuation through a phosphoric oxide tube. The only impurity present in the first specimen analysed below was a small amount of the dark blue tetrahydrate, and in the second, very small amounts of both the dark blue and the white modifications:

(I) 12.405 lost 0.993. $\text{H}_2\text{O} = 8.00$. (II) 33.823 lost 3.220.
 $\text{H}_2\text{O} = 9.52$.

$\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ requires loss of $1\text{H}_2\text{O} = 9.23$ per cent.

The Light Green Dihydrate, $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$.—When water was pumped off from crystals of the tetrahydrate at a temperature between 70° and 80° , this dihydrate resulted, and further evacuation at 100° had no effect; the only impurity was a small amount of the anhydrous, white chromous chloride, CrCl_2 :

(I) 22.354 lost 4.165. $\text{H}_2\text{O} = 18.63$. (II) 11.995 lost 2.383.
 $\text{H}_2\text{O} = 19.86$. (III) 12.654 lost 2.391. $\text{H}_2\text{O} = 18.89$.

$\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ requires loss of $2\text{H}_2\text{O} = 18.48$ per cent.

Anhydrous White Chromous Chloride, CrCl_2 .—This was prepared from the tetrahydrate by exposing the crystals to a temperature of 180° in a vacuum. After determining the loss of water, gravimetric analyses of the chlorine present in the second specimen were carried out; the results gave $\text{Cl} = 55.2$ and 55.6 , whilst CrCl_2 requires $\text{Cl} = 57.6$ per cent., showing that very little hydrogen chloride had escaped;

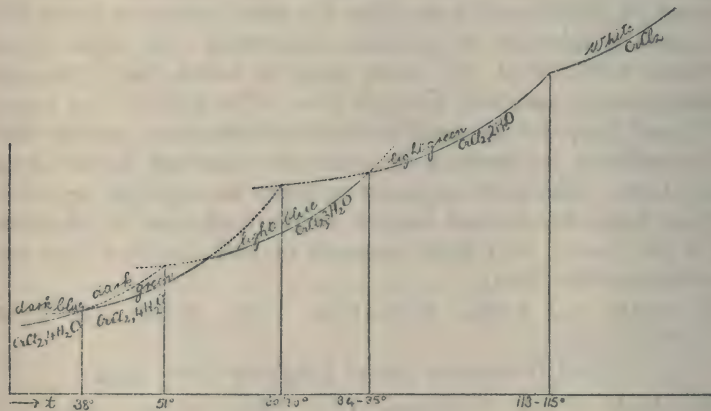
(I) 22.354 lost 8.340. $\text{H}_2\text{O}=37.31$. (II) 12.654 lost 4.542. $\text{H}_2\text{O}=35.89$.

$\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ requires loss of $4\text{H}_2\text{O}=36.96$ per cent.

With regard to the conditions of existence of the various modifications described above, the following relationships were established by direct qualitative observation:

A. *In the Presence of Solution*.—The dark blue $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ is the stable modification up to a temperature of 38° ; it then passes into the dark green $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$, but if the dark green hydrate does not appear, the dark blue modification is stable up to 51° , at which temperature it is replaced by pale blue $\text{CrCl}_2 \cdot 3\text{H}_2\text{O}$. The dark green tetrahydrate is stable between 38° and 60 — 70° , and then turns into the light green dihydrate $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$. The pale blue trihydrate $\text{CrCl}_2 \cdot 3\text{H}_2\text{O}$ is converted into light green dihydrate $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$ at

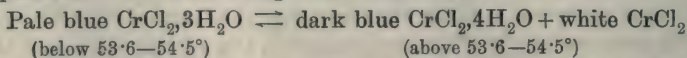
FIG. 1.



84 — 85° , and this in turn becomes white anhydrous chromous chloride CrCl_2 at 113 — 115° .

The accompanying diagram exhibits these relationships, and represents any property (for example, concentration) of the saturated solutions plotted against the temperature. The observed regions of metastable equilibria are represented by dotted parts of the curves.

B. *Under the Vapour Tensions of the Hydrates Themselves*.—The phase rule demands three simultaneous phases at every equilibrium temperature. The following was established:



The dark blue tetrahydrate is recognised at once by its indigo surface colour. The pale blue trihydrate is not instantaneously converted into dark blue tetrahydrate by water; the boundary line

moves at the rate of 2 cm. per hour at 17° in a caked mass of wet crystals which are passing into dark blue crystalline tetrahydrate.

The Isomerides in Solution.

The solution is green when hot, concentrated, and acid; blue when cold or dilute. The colour change requires only a few seconds in neutral solution, even at the ordinary temperature, but the presence of acid reduces this velocity enormously, so that the colour change may require weeks for completion. The dark green $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ dissolves to give a green solution; the others produce a blue solution at once.

The two alternative explanations of the structural difference, which has thus been shown to be independent of the state (solid or solution), are the following:

(a) Partial hydrolysis, with the formation of CrOH^+ as a green cation.

(b) Partial dissociation, forming a green complex ion CrCl^+ incapable of further dissociation.

Hypothesis (a) is irreconcilable with the fact mentioned by Prud'homme, and confirmed by ourselves, that concentrated hydrochloric acid favours the formation of the green colour; (b) requires that the addition of another chloride would favour the green colour. This was the case when large quantities of potassium chloride were added to a hot solution. This consequently appears to be the most probable explanation, and is analogous to corresponding cases in the chromic salts.

Determination of Vapour Tension.

The tensimeter measurements were carried out in an apparatus of the usual type (with several joints inserted in the bulbs to prevent dislodgement of the chromous chloride powder). Mercury was used as manometer liquid, and the height of this was read on a standard glass scale by a telescope fitted with a micrometer eyepiece. The other bulb contained concentrated sulphuric acid, or was simply evacuated by means of a Toepler pump. The following are the final results obtained after an extended series of measurements.

Experiment I.

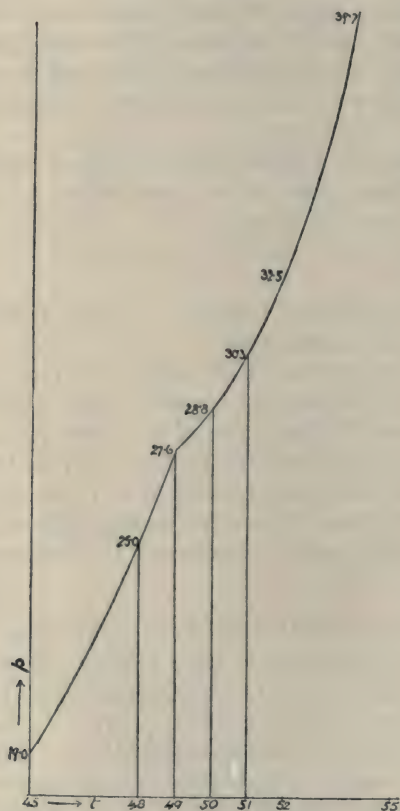
Pale blue $\text{CrCl}_2 \cdot 3\text{H}_2\text{O}$ + saturated solution (above 49°).

Dark blue $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ + pale blue $\text{CrCl}_2 \cdot 3\text{H}_2\text{O}$ (below 49°).

Temp.	Pressure, mm.	Temp.	Pressure, mm.
25°	2·9	51°	30·3
35	8·0	52	32·5
45	19·0	55	39·7
48	25·0	60	56·0
49	27·6	65	78·4
50	28·8		

The results obtained between 45° and 55° are plotted in the accompanying figure, in order to show the very distinct break in the curve at 49.0° , where the dark blue, crystalline tetrahydrate decomposes into pale blue crystals and saturated solution of the trihydrate. Hence the transition temperature is 49.0° , in good

FIG. 2.



agreement with the value 51° found by direct observation in the preceding part of the paper.

Experiment II.

Light green $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$ + saturated solution (above $84-85^{\circ}$).

Pale blue $\text{CrCl}_2 \cdot 3\text{H}_2\text{O}$ + light green $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$ (below $84-85^{\circ}$).

Temp.	Pressure, mm.	Temp.	Pressure, mm.
12.5°	0.08	75.0°	147.7
50.0	28.5	76.0	150.1
60.2	56.4	77.0	163.1
65.0	79.3	79.5	182.3
70.0	108.0		

If these vapour tensions are plotted, it is seen that the curve is quite smooth up to the highest temperature, thus showing that the transition point, where only $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$ in contact with its saturated solution would remain, must lie still higher; according to the data given on p. 90, this transition point lies between 84° and 85° .

These results were confirmed by dilatometer measurements, starting with crystals of the blue tetrahydrate and its saturated solution, and using paraffin oil as dilatometer liquid:

Time at constant temperature.				Time at constant temperature.			
Temp.	Min.	Height.	Remarks.	Temp.	Min.	Height.	Remarks.
86.4°	30	56.00		81.1°	5	48.00	Temperature had been previously raised to 86° for 5 minutes, and then lowered to 81.1° . The meniscus fell steadily, and was still falling.
85.1°	25	54.38		81.1°	10	47.10	
84.0°	15	53.05	rising	81.1°	15	46.61	
84.0°	20	53.20		81.1°	25	45.55	falling slowly
79.0°	5	46.08	falling rapidly	81.1°	30	45.02	
79.0°	10	44.45		82.0°	5	45.25	
79.0°	20	41.50		82.0°	15	45.20	
79.0°	30	41.12		82.0°	25	45.18	
80.0°	5	42.73	falling				
80.0°	15	42.71					
80.0°	20	42.60					

From the above experiment, it is evident that the transition point, above which pale blue trihydrate $\text{CrCl}_2 \cdot 3\text{H}_2\text{O}$ turns into light green dihydrate $\text{CrCl}_2 \cdot 2\text{H}_2\text{O}$ in contact with saturated solution, is $82\text{--}84^\circ$, in agreement with the value $84\text{--}85^\circ$ obtained by direct observation. No further determinations with tensimeter or dilatometer were undertaken, as the present confirmations of these two numbers suffice to show the trustworthiness of the other directly observed values.*

* The authors are indebted to the kindness of C. W. Spiers of this department for analyses of the specimens which had been used in the tensimeter and dilatometer experiments. These analyses were carried out nine months after the above experiments had been performed, during which time the tensimeter had been untouched, and the substance in the dilatometer bulb had been protected from the atmosphere by the layer of paraffin oil used in the stem as indicating liquid. The contents of the tensimeter were analysed by measuring the volume of oxygen absorbed, followed by gravimetric determination of the whole of the chromium present. The result showed that, after all this time, the crystals in the tensimeter contained 97.96 per cent. of pure chromous chloride.

The analysis of the substance in the dilatometer was carried out both by the method of oxygen absorption and by the reduction of iodine solution, followed in each case by gravimetric determination of the total chromium present. The absorption of oxygen showed that 98.4 per cent. of the chromium was present in the chromous condition, whilst two iodine determinations performed indicated a purity

Depression of the Freezing Point by the Isomerides in Solution.

The Blue Solution.—The freezing-point determinations were carried out in a modification of a Beckmann apparatus, employing a stirrer, in an atmosphere of hydrogen at barometric pressure. The concentration of the solution was determined after the experiment by a gravimetric determination of the chlorine:

Concentration (g.-mol. in 1000 g. H ₂ O).	Lowering.	Dissociation per cent.
0.1996	1.059°	93
0.1037	0.526	87

The apparent increase in dissociation in the stronger solution is usual where the lowering is so great.*

The Green Solution.—All attempts to prepare a specimen of the dark green $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ previously described proved unavailing; hence, in order to obtain the green solution of chromous chloride, a small quantity of the dark blue tetrahydrate was heated for three days to 95° with a quantity of water just insufficient to dissolve it, to which a few drops of concentrated hydrochloric acid had been added. The arrangements for determining the freezing point were exactly the same as in the case of the blue solution, but the solution was prepared by adding *N*/10-hydrochloric acid in this case. The freezing point of this dilute green solution having been determined, the solution was analysed (1) for chromium and (2) for chlorine. From the results of the analyses, the amount of hydrochloric acid in the solution was calculated; a hydrochloric acid solution of this strength was then made, and its freezing point determined. The difference between the two freezing points gave the lowering due to the chromous chloride in the solution:

Concentration (g.-mol. in 1000 g. of water).		Lowering caused by CrCl_2 .	Dissociation per cent.
CrCl_2 .	HCl.		
0.1690	0.1183	0.771°	73
0.0182	0.1441	0.083	72

The agreement between these two sets of experiments is fortuitous, since it is certain from the method of preparation that the solutions of 104.4 and 95.5 per cent. respectively. Gravimetric determination was rather difficult here on account of the presence of the dilatometer oil.

It is obvious that in any case the presence of even appreciable amounts of the excessively soluble chromic salts, CrCl_3 or CrOHCl_2 , in solution could have no possible influence on dilatometric determinations, since such depend solely on the abrupt alteration in volume of the solid present.

* Out of 22 cases of halogen compounds of bi- and ter-valent metals, for which data are given in Landolt-Börnstein's tables, 20 behave as thus mentioned.

contained blue chromous chloride in addition to the green isomeride. The dissociation is calculated, as in the preceding table, assuming the formula CrCl_2 (dissociating into three ions). It is obvious that the green solution is much less dissociated than the blue isomeride, although markedly so. This result agrees with the formula $\text{CrCl}\cdot\text{Cl}$, which represents the green isomeride as dissociating into two ions.

Our thanks are due to Dr. J. W. McBain, at whose suggestion this work was undertaken, for the continued interest he took in it.

THE CHEMICAL DEPARTMENT,
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XI.—*Reactivity of the Halogens in Organic Compounds. Part V. Interaction of Esters of the Bromo-substituted Fatty Acids with Silver Nitrate in Alcoholic Solution.*

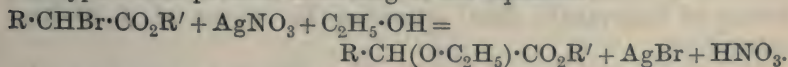
By GEORGE SENTER.

IN a previous paper (Trans., 1910, **97**, 346) the results of an experimental investigation of the rate of interaction of silver salts with the lower members of the bromo-substituted fatty acids and their sodium salts in aqueous solution have been communicated. In the case of the acids, the reaction is represented by the general equation:



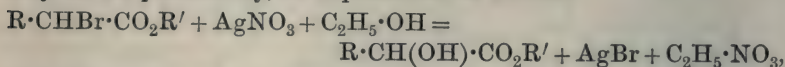
where R represents hydrogen or an alkyl group. It was shown that the rate of reaction increases very considerably with increasing complexity of the group R, and, further, that the reactions are markedly accelerated by silver bromide.

The present communication is mainly concerned with the kinetics of the reactions between silver nitrate and the methyl and ethyl esters of α -bromoacetic, α -bromopropionic, α -bromobutyric, α -bromoisobutyric, and α -bromoisovaleric acids in ethyl alcohol, and in some cases in methyl alcohol. It might be anticipated that reactions of this type would proceed according to the equation:



It was found, however, that the amount of nitric acid formed is not equivalent to the silver nitrate used up—with ethyl bromo-

propionate only 50 per cent. of the silver nitrate reappears as nitric acid—and a second reaction must therefore be taking place. This may, in all probability, be represented as follows:



and the total change is therefore rather complicated. The evidence for the view that two simultaneous reactions occur is that the production of nitric acid formed to silver nitrate used up remains constant throughout the reaction within the limits of experimental error (p. 99).

In striking contrast to the behaviour of the free acids in aqueous solution (*loc. cit.*), the rate of reaction with the esters diminishes regularly with increasing complexity of the alkyl group R. On the other hand, the substitution of a methyl group for hydrogen in the ester group R' tends to accelerate the change. A few measurements have also been made in mixtures of alcohol and water, and the effect of indifferent substances, such as acetone, chloroform, and glycerol, on the rate of reaction has been investigated. Under comparable conditions, the reactions are rather more rapid in methyl than in ethyl alcohol.

Units and Method of Measurement.

The ethyl alcohol used in the experiments was dehydrated by boiling for some days with freshly ignited lime, and finally with metallic calcium. Traces of reducing substances (aldehydes) were removed by distilling the alcohol from dry silver nitrate. Density determinations showed that the alcohol thus prepared was entirely free from water. The methyl alcohol was obtained from Kahlbaum, and was dehydrated by the method used for ethyl alcohol.

The esters were obtained from Kahlbaum, and were tested as regards purity. The esters of bromoacetic and bromopropionic acids were found to be pure; those derived from the higher acids were subjected to fractional distillation, and portions boiling at constant temperature used in the experiments.

The measurements were carried out as described in the previous paper. The solutions were warmed separately in the thermostat, and then mixed in a number of small tubes. In all cases the volume of reaction mixture in each tube measured 12 c.c. At definite times the contents of a tube were transferred to a beaker containing a slight excess of *N*/50-ammonium thiocyanate, and the excess of thiocyanate then estimated by means of *N*/50-silver nitrate.

Unless otherwise stated, the velocity coefficients are calculated by means of the equation for a bimolecular reaction, which, for

equivalent quantities, has the form $kt = x/a(a-x)$, where the symbols have the usual significance. In the above equation, $a-x$ represents the number of c.c. of $N/50$ -thiocyanate equivalent to the amount of silver nitrate in 12 c.c. of the reaction mixture. The velocity coefficients in the tables refer therefore to a concentration of $1/12 \times 50$ mols. per litre, and, if it is required to refer them to a concentration of 1 mol. per litre, they must be multiplied by 600. The unit of time is one minute throughout. The majority of the experiments were made at 49.9° ; a few at 26.0° .

The Esters in Ethyl Alcohol as Solvent.

Two or three entirely independent series of measurements were made with each ester, the results being very concordant. Only a few typical results are recorded in the accompanying tables.

TABLE I.

Temperature 49.9° .

Methyl bromoacetate, $N/10$. Silver nitrate, $N/20 \times 0.99$.			Ethyl bromoacetate, $N/10$. Silver nitrate, $N/20 \times 0.99$.		
t (min.).	$a-x$.	$k \times 10^4$.	t (min.).	$a-x$.	$k \times 10^4$.
0	29.6	—	0	29.6	—
60	27.7	0.190	60	27.5	0.208
180	24.2	0.196	180	23.9	0.208
360	20.3	0.192	360	19.7	0.207
1440	8.8	0.180	1440	8.0	0.197

Methyl bromopropionate, $N/10$. Silver nitrate, $N/20 \times 0.99$.			Ethyl bromopropionate, $N/10$. Silver nitrate, $N/20 \times 0.99$.		
t (min.).	$a-x$.	$k \times 10^4$.	t (min.).	$a-x$.	$k \times 10^4$.
0	27.85	—	0	27.7	—
180	25.65	0.075	120	26.0	0.092
420	23.20	0.073	360	23.2	0.085
660	21.20	0.073	1200	16.2	0.085
			2520	9.7	0.086

Propyl bromopropionate, $N/10$. Silver nitrate, $N/20 \times 0.99$.			Ethyl bromobutyrate, $N/10$. Silver nitrate, $N/20 \times 0.99$.		
t (min.).	$a-x$.	$k \times 10^4$.	t (min.).	$a-x$.	$k \times 10^4$.
0	27.7	—	0	28.45	—
330	23.7	0.087	120	27.65	0.040
1170	16.55	0.087	300	26.60	0.038
2610	9.7	0.085	1380	21.55	0.037
			2820	17.00	0.035

Ethyl bromoisobutyrate, $N/10$. Silver nitrate, $N/20$.			Ethyl bromoisovalerate, $N/10$. Silver nitrate, $N/20 \times 0.99$.		
t (min.).	$a-x$.	$k \times 10^4$.	t (min.).	$a-x$.	$k \times 10^4$.
0	28.5	—	0	28.7	—
120	27.3	0.063	180	27.9	0.026
300	25.6	0.062	1140	24.9	0.022
1260	19.3	0.059	2580	22.1	0.019
2700	13.8	0.057			

In examining the above results, it will be noticed that the concentrations of silver nitrate corresponding with $t=0$ are in some cases considerably less than 30 c.c., which is the value for 12 c.c. of a $N/20$ -solution of silver nitrate. In these reactions, $t=0$ is not the time of mixing the solutions, but corresponds with a somewhat later stage of the reaction, in order to eliminate the effect of initial disturbances.

TABLE II.

Temperature 26.0°.

Methyl bromoacetate, $N/10$	}	$a-x$ from 29.3 to 25.0 in 1275 minutes.	$k \times 10^4 = 0.021$.
Silver nitrate, $N/20$			
Methyl bromopropionate, $N/10$	}	$a-x$ from 29.3 to 24.2 in 4080 minutes.	$k \times 10^4 = 0.0086$.
Silver nitrate, $N/20$			

Methyl Alcohol as Solvent.

TABLE III.

Temperature 49.9°.

Methyl bromoacetate, $N/10$. Silver nitrate, $N/20$.			Ethyl bromobutyrate, $N/10$. Silver nitrate, $N/20$.		
t .	$a-x$.	$k \times 10^4$.	t .	$a-x$.	$k \times 10^4$.
0	26.0	—	0	27.7	—
120	22.35	0.230	120	26.4	0.069
300	18.0	0.230	300	24.65	0.068
1260	7.4	0.217	1380	17.15	0.066
2700	2.3	0.217	2820	11.70	0.062

Solvent: 95 per cent. Alcohol by Volume.

TABLE IV.

Methyl bromopropionate, $N/10$. Silver nitrate, $N/20$.

Temperature 26.0°.			Temperature 49.9°.		
t .	$a-x$.	$k \times 10^4$.	t .	$a-x$.	$k \times 10^4$.
0	27.8	—	0	29.5	—
120	25.5	0.083	1260	27.45	0.0096
420	23.1	0.079	2640	25.6	0.0093
660	20.8	0.080	4080	23.9	0.0093

Solvent: 50 per cent. Alcohol by Volume.

TABLE V.

Methyl bromoacetate, $N/10$. Silver nitrate, $N/20$. Temperature 26.0°.			Ethyl bromoacetate, $N/10$. Silver nitrate, $N/20$. Temperature 49.9°.		
t (min.).	$a-x$.	$k \times 10^4$.	t (min.).	$a-x$.	$k \times 10^4$.
0	29.5	—	0	29.6	—
1220	27.3	0.0109	120	27.5	0.103
2640	24.8	0.0114	360	24.2	0.097

Ethyl Alcohol with 50 per cent. Acetone, Chloroform, and Glycerol respectively as Solvents.

TABLE VI.

Ethyl bromoacetate, <i>N</i> /10.		Silver nitrate, <i>N</i> /20.		Temperature 49.9°.	
Solvent.	100 per cent. alcohol.	50 per cent. acetone.	50 per cent. chloroform.	50 per cent. glycerol.	
Change of $\alpha - x$	29.6 - 8.0	29.9 - 17.6	29.9 - 20.5	29.9 - 18.1	
$k \times 10^4$	0.208 - 0.197	0.200 - 0.166	0.148 - 0.115	0.061 - 0.048	

Finally, the results of a series of experiments designed to find what proportion of the silver nitrate appears in the products as nitric acid is given in the accompanying table. A number of tubes containing ethyl bromopropionate and silver nitrate in absolute alcohol were placed in the same thermostat, and simultaneous titrations of the silver nitrate with thiocyanate and of the nitric acid with *N*/20-sodium hydroxide, using phenolphthalein as indicator, were made. The results, referred to the same standard of concentration, are as follows:

TABLE VII.

t (min.)	AgNO ₃ used up.	HNO ₃ formed.	Ratio HNO ₃ /AgNO ₃ .
0	0.0	0.0	—
120	1.8	0.9	50 per cent.
360	4.5	2.3	51 „
660	7.3	3.6	49 „
1440	15.2	7.5	49 „

The figures show that within the limits of experimental error 50 per cent. of the silver nitrate is changed to nitric acid, and the ratio remains constant throughout the reaction. It should be stated that owing to the presence of precipitated silver bromide, the end-point in titrating nitric acid with sodium hydroxide is not quite sharp, and a correction had to be applied.

Summary and Discussion of Results.

(1) *General Character of the Reactions.*—The data quoted in tables I—VII show that the reactions are represented fairly satisfactorily by an equation of the second order, although there is a slight tendency for the velocity-coefficients to diminish as the reactions proceed. In contrast to the behaviour of the acids (*loc. cit.*), the nitric acid formed has only a slight retarding effect, and the catalytic action of the precipitated silver bromide, which is so pronounced in aqueous solution, is also relatively unimportant in alcoholic solution.

The effect of changing the solvent presents several interesting

features. The ratio of the velocity-coefficients for methyl bromopropionate in 100 per cent., in 95 per cent., and in 50 per cent. ethyl alcohol (with water) is 73:93:37 (the last figure is not given in the tables), so that the addition of a little water accelerates the reaction, whilst a greater proportion retards it. A similar observation was made by Miss Burke and Donnan (*Zeitsch. physikal. Chem.*, 1909, **69**, 163) for the reaction between silver nitrate and methyl iodide, but so far no plausible explanation of this behaviour has been suggested. It will be observed that in the mixtures with 50 per cent. alcohol, there is a tendency for the coefficients to increase during the reaction. This is doubtless due to partial hydrolysis of the ester in the presence of nitric acid; free bromoacetic acid reacts with silver nitrate rather more rapidly than the corresponding ester (table VIII).

The ratio of the initial velocity-coefficients with ethyl bromoacetate in 100 per cent. alcohol and in mixtures with 50 per cent. of acetone, chloroform, and glycerol respectively is 208:200:148:61 (table VI). This is also the order of increasing viscosities of the solvents, and it is probable that this is the chief factor concerned.

In all cases, the reactions were found to proceed faster in methyl than in ethyl alcohol (tables I and III). For methyl bromoacetate, the ratio is only 1.15:1, but for ethyl bromobutyrate is about 1.8:1. Burke and Donnan obtained similar results with the alkyl halogen compounds and silver nitrate, but express no opinion as to the reasons for this behaviour. It is probably also mainly a viscosity effect, the ratio of the viscosities of methyl and ethyl alcohol at 50° being about 1:1.7.

(2) *Effect of Temperature of Reaction Velocities.*—From a comparison of the data in tables I and II, it is clear that an elevation of temperature from 26° to 49.9° increases the rate of reaction for both methyl bromoacetate and methyl bromopropionate about nine times, so that the temperature-coefficient for 10° is about 2.5. The same value is obtained for methyl bromopropionate in 95 per cent. alcohol.

(3) *Comparison of the Reactivity of Acids and Esters.*—In a previous paper (*loc. cit.*) the rate of reaction of the lower bromo-substituted fatty acids with silver nitrate in aqueous solution has been measured. Since then the speed of the same reactions has been measured in ethyl alcohol, and the results will be communicated in a later paper. A complication arises in this case from the fact that the nitric acid formed in the course of the reaction exerts a very considerable retarding action, much more pronounced even than in aqueous solution (Sener, *loc. cit.*, p. 351), and it is therefore difficult to give a satisfactory velocity-coefficient for these reactions.

It is, however, a matter of considerable interest to compare the reactivities of the acids and esters, and this is done in table VIII, where the velocity-coefficients for the acids are those very near the beginning of the reaction, before the nitric acid has accumulated to any great extent in the system. The coefficients in the accompanying table are expressed in the same units as those used in the present paper, and were all determined under corresponding conditions at 26°:

TABLE VIII.

	$\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}.$	$\text{CHMeBr}\cdot\text{CO}_2\text{H}.$	$\text{CHEtBr}\cdot\text{CO}_2\text{H}.$	
$k \times 10^5$	0.51 [8.0]	18 [324]	—	in ethyl alcohol
$k \times 10^5$	0.55 [8.8]	55 [880]	250 [4000]	in water ,,
	$\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Me}.$	$\text{CHMeBr}\cdot\text{CO}_2\text{Me}.$	$\text{CHEtBr}\cdot\text{CO}_2\text{Me}.$	
$k \times 10^5$	0.21 [3.3]	0.086 [1.3]	0.066 [1]	in ethyl alcohol ,,

The numbers in brackets represent the relative rates of the reactions referred to the slowest, that between methyl bromobutyrate and silver nitrate in ethyl alcohol, as unity.

An examination of the table shows the interesting fact that the reactivities of bromoacetic acid and its methyl ester are of the same order in ethyl alcohol, but when bromopropionic acid and its ester are compared, there is seen to be an enormous difference in the speed with which the bromine is displaced. For reasons given in an earlier paper, however, it appears that the reactions of the bromo-substituted fatty acids with silver nitrate are abnormal, and cannot be compared with the corresponding reactions with the esters. For the same reason, it is probable that most of the instances in the literature in which the relative reactivities of acids and esters are regarded merely as showing the effect of substituting a methyl group for a hydrogen atom, are of no value whatever from this point of view.

(4) *Relative Reactivities of the Esters in Ethyl Alcohol.*—The relative activities of the esters, as expressed by the velocity-coefficients of the reactions with silver nitrate under corresponding conditions (table I), are summarised in table IX:

TABLE IX.

Ester.	$k \times 10^4.$
Ethyl bromoacetate..	0.208
,, α -bromopropionate	0.085
,, α -bromoisobutyrate	0.062
,, α -bromobutyrate	0.038
,, α -bromoisovalerate	0.022
Methyl bromopropionate.....	0.077
Ethyl	0.085
n-Propyl	0.087

These results may be summed up in the statement that, in a compound of the type $R \cdot CHBr \cdot CO_2R'$, the successive displacement of hydrogen in the group R by methyl groups lessens the reactivity of the bromine towards silver nitrate, but, as regards the group R' , the ethyl ester is rather more reactive than the methyl ester, while the reactivity of the ethyl and propyl esters is the same. It is of interest to note that this order of reactivity of the ethyl esters of bromo-substituted acids exactly corresponds with that found by Reicher (*Annalen*, 1885, **228**, 257) for the saponification of the ethyl esters of the acids themselves by sodium hydroxide. This agreement even extends to the relative reactivity of the butyric and isobutyric esters, although ethyl butyrate is saponified only a very little less rapidly than ethyl isobutyrate. Slator and Twiss (*Trans.*, 1909, **96**, 93) find that the reactivity of the bromo-substituted esters, measured with regard to sodium thiosulphate, is the same as that given in the present paper, with the exception that ethyl α -bromobutyrate is considerably more reactive than the corresponding isobutyrate.

It appears justifiable to ascribe the relative reactivity in the above instances mainly to steric hindrance. The strength of the linking between bromine and the rest of the molecule is doubtless affected to some extent by substitution, but this influence is probably negligible in comparison with the steric effect.

As regards the effect of substitution in the group attached to the oxygen, Slator and Twiss (*loc. cit.*) and Clarke (*Trans.*, 1910, **97**, 416) also find by different methods that the bromine in ethyl bromoacetate is more reactive than that in methyl bromoacetate. As the magnitude of the effect is not greatly beyond the limits of possible experimental error, the possibility was taken into account that the methyl ester might have been converted into the ethyl ester under the influence of the ethyl alcohol used as solvent (compare Purdie, *Trans.*, 1885, **47**, 862; 1887, **51**, 627; 1888, **53**, 391), but the facts (1) that the ratio of the velocities for the two esters is independent of the time during which they remain dissolved in the alcohol before the reaction, and (2) that the ratio of the velocity-coefficients remains constant during the reaction, appear completely to dispose of this suggestion.

Further, it has to be remembered, in connexion with the relative magnitude of the effect, that ethyl bromoacetate is derived from the methyl compound by substitution in the δ -position with regard to the bromine, whereas ethyl bromopropionate is derived from ethyl bromoacetate by substitution in the β -position. The observations appear to be accounted for most satisfactorily on the basis of the views as to the effect of substituents on the degree

of affinity, developed by Flürscheim (*J. pr. Chem.*, 1905, [ii], **71**, 497; 1907, **76**, 165, 185).

(5) *Internal Mechanism of the Reactions*.—As the total effect is the sum of two simultaneous reactions, and the matter is therefore rather complicated, there is nothing to be gained by discussing the possible mechanism in detail at the present stage. As the order of reactivity of the esters with two such different substituents as silver nitrate and sodium thiosulphate is substantially the same, it appears probable that the reaction is one of direct substitution, the place of the bromine removed by the silver being instantaneously taken by a hydroxy- or ethoxy-group. Euler (*Ber.*, 1906, **39**, 2726) has suggested that in reactions of this type complex ions, containing silver and halogen, play an important part, but there is no direct evidence in favour of this view, and it does not appear to present any advantage over that of direct substitution.

In conclusion, I desire to express my most sincere thanks to Mr. T. J. Ward, of St. Mary's Hospital Medical School, for valuable assistance in the experimental part of the work, and also to the Research Fund Committee of the Chemical Society for a grant which has defrayed most of the expense of the investigation.

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XII.—*Studies in the Carbazole Series.*

By CARL GUSTAV SCHWALBE and SALOMON WOLFF.

THE object of this research was to prepare mercaptans of carbazole with the intention of converting them into sulphide dyes. For this purpose we have investigated several possible methods of preparation, but in most cases have found that, instead of obtaining the required mercaptan, the derivatives employed were reconverted into carbazole itself.

In the first place, we endeavoured to prepare carbazole mercaptan from 3-aminocarbazole by means of the diazo-reaction. This compound was diazotised and treated with copper powder and sulphurous acid, and later also with copper thiocyanate paste. We were not successful in isolating a mercaptan from the products of reduction, but obtained instead carbazole itself. We also proved that the latter is formed on boiling a solution of diazotised 3-aminocarbazole,

or by treating such a solution with cuprous chloride, according to Sandmeyer.

Another possible method of preparing such mercaptans, namely, by the reduction of the sulphonyl chlorides, cannot, in the case of carbazole, be applied, since the monosulphonic acids are at present unknown. We have, however, closely examined the reduction products of the di- and tri-sulphonic acids of carbazole, prepared according to Schultz and Hauenstein's method (*J. pr. Chem.*, 1907, [ii], 76, 336), but we have only obtained very small quantities of an impure substance with mercaptan-like properties, although we have varied the experimental conditions in many ways.

It was not improbable that monosulphonic acids of carbazole, on reduction, would behave differently from the disulphonic acids, and we accordingly carried out a great number of different sulphonating experiments, always obtaining, however, disulphonic acids, of which we identified two new isomerides.

Furthermore, if both nuclei in carbazole are symmetrically sulphonated, it might be possible that, on introducing, for example, a nitro-group into one nucleus, the other nucleus would take up a single sulphonic acid group, and only a monosulphonic acid would be obtained. On reduction, diazotisation, and boiling with alcohol, such a nitrocarbazolemonosulphonic acid might be expected to yield a carbazolemonosulphonic acid.

We accordingly sulphonated 3-nitrocarbazole, but did not obtain a monosulphonic acid, so that this method also could not be used.

Carbazole may be synthetically prepared from phenylbenzotriazoles according to Graebe and Ullmann (*Annalen*, 1896, 291, 16), and we have attempted to apply a modification of this synthesis to the preparation of a monosulphonic acid by making use of *o*-nitrodiphenylamine-*p*-sulphonic acid. This should be convertible into the corresponding azimino-compound, and the latter into a carbazolemonosulphonic acid. We succeeded, in fact, in preparing 1-phenyl-1:2:3-benzotriazole-5-sulphonic acid, but, on heating it, obtained carbazole itself instead of the expected monosulphonic acid. It would therefore seem that at the high temperature of formation the monosulphonic acid of carbazole decomposes, with formation of carbazole. In further support of this, we have shown that on heating the salts of the disulphonic acids of carbazole at a high temperature, carbazole is regenerated. Schultz and Hauenstein have also proved that the potassium salt of a disulphonic acid of carbazole, on being heated with potassium cyanide, gave rise to carbazole. From these data it seems clear that certain of the carbazole derivatives show in their reactions a strong tendency to regenerate carbazole, and that the ordinary transformations

which occur readily in the benzene series do not here take place.

EXPERIMENTAL.

3-Aminocarbazole.

Ruff and Stein (*Ber.*, 1901, **34**, 1677) obtained 3-aminocarbazole on reducing nitronitrosocarbazole with stannous chloride and hydrochloric acid. We modified this method by using technical sodium sulphide. Nitronitrosocarbazole is mixed with 10 parts of 96 per cent. alcohol, and to this mixture 10 parts of concentrated sodium sulphide solution are added. A deep red coloration is produced, and the mixture has an ammoniacal odour. The product is heated on the water-bath until a sample of the mixture no longer gives a red colour with aqueous sodium sulphide. As intermediate product, a substance, melting at 210° , was isolated, which was probably identical with nitrocarbazole. The methods described in D.R.-P. 122852 and 134983, and also that recommended by Ziersch (*Ber.*, 1909, **42**, 3797), namely, reduction with sodium hyposulphite, led, in our experiments, to less pure products.

Carbazoledisulphonic Acids.

Schultz and Hauenstein heated carbazole with the quantity of concentrated sulphuric acid necessary for the formation of a monosulphonic acid, at a temperature of from 70° to 75° during six to seven hours. After conversion into the barium salt, these authors obtained a separation of crystals only after the concentrated solution had been kept for a long time, but the barium salt prepared by us crystallised out directly on cooling the solution, as a voluminous, colourless mass. On reconvertng this barium salt into the potassium salt, and treating the latter with phosphorus pentachloride, a *disulphonyl chloride* was obtained, which crystallised from acetone in colourless leaflets, and gave, with ammonia, unlike Schultz and Hauenstein's product, a *disulphonamide*, having no definite melting point.

When heated under pressure with 48 per cent. sulphuric acid at 120° , or with water at 130° , the potassium salt of this acid gives rise to carbazole.

The *disulphonyl chloride* gave on analysis:

0.1488 gave 0.123 AgCl. Cl=20.45.

0.1668 „ 0.2058 BaSO₄. S=16.92.

C₁₂H₇O₄NCl₂S₂ requires Cl=19.50; S=17.58 per cent.

Analysis of the *disulphonamide* furnished the following numbers:

0.175 gave 0.2518 BaSO₄. S=19.76.

0.148 „, 16.5 c.c. N₂ at 21° and 750 mm. N=12.97.

C₁₂H₁₁O₄N₃S₂ requires S=19.69; N=12.92 per cent.

Carbazole is readily sulphonated on treatment with mono-potassium disulphate, KH₃(SO₄)₂, at about 100°. The potassium salt of the sulphonic acid formed proved to be a mixture of di- and tri-sulphonic acids.

We have also found that carbazole is easily sulphonated by 67 per cent. sulphuric acid.

Ten grams of carbazole are heated with 50 c.c. of 67 per cent. sulphuric acid at 115° for some hours, the mixture being stirred. By this process a fairly soluble barium salt and a crystalline *potassium* salt of *carbazoledisulphonic acid* are produced. The *disulphonyl chloride* melts at 102°, reacts in the cold with ammonia, giving a yellow coloration, and finally dissolves, but a disulphonamide could not be obtained.

On heating the potassium salt with 48 per cent. sulphuric acid or with water under pressure, it remains unaltered, and in this respect also differs from the above-described disulphonic acid, which regenerates carbazole.

On analysis of the *potassium* salt:

0.1500 gave 0.1628 BaSO₄. S=15.20.

0.1500 „, 0.1630 BaSO₄. S=15.21.

C₁₂H₇O₆NS₂K₂ requires S=15.88 per cent.

The *disulphonyl chloride* was also analysed:

0.1520 gave 0.1218 AgCl. Cl=19.83.

0.1520 „, 0.1214 AgCl. Cl=19.76.

C₁₂H₇O₄NCl₂S₂ requires Cl=19.50 per cent.

Thus the existence of at least two isomeric disulphonic acids is shown by these experiments. The difference in properties exhibited by the acid prepared by us by Schultz and Hauenstein's method cannot as yet be satisfactorily explained.

Sulphonation of 3-Nitrocarbazole.

Five grams of 3-nitrocarbazole were heated with 25 c.c. of 67 per cent. sulphuric acid at 130—140° until dissolved. After separation of a tarry by-product, the filtrate was treated with barium carbonate, and a yellow, amorphous *barium* salt was isolated, which could not be obtained crystalline:

0.928 gave 0.3832 BaSO₄. Ba=24.30.

0.1554 „, 0.1270 BaSO₄. S=11.22.

C₁₂H₆O₈N₂S₂Ba requires Ba=26.95; S=12.62 per cent.

These results indicate that a mixture of mono- and di-sulphonic acid is formed.

On reducing the nitrocarbazolesulphonic acid by Claisen's method, a small quantity of a silver-grey *potassium 3-aminocarbazoledisulphonate* was isolated:

0.1436 gave 8.2 c.c. N_2 at 22° and 747 mm. $N = 6.4$.

$C_{12}H_8N_2O_6S_2K_2$ requires $N = 6.7$ per cent.

1-Phenyl-1:2:3-benzotriazole-5-sulphonic Acid.

This acid was obtained by the diazotisation of *o*-aminodiphenylamine-*p*-sulphonic acid. The latter was prepared by the action of aniline on *p*-chloro-*m*-nitrobenzenesulphonic acid, and reduction of the *o*-nitrodiphenylaminesulphonic acid formed.

o-Aminodiphenylaminesulphonic acid is described in the literature as an indistinctly crystalline solid. We obtained it in well-defined slightly violet needles.

On diazotisation, a red solution was obtained, which did not combine with phenols. On evaporation of this, a brown, amorphous substance separated out, which, on being slightly heated on platinum foil, swells up and leaves a grey, iridescent mass. On slowly heating this triazole at 390 — 400° , carbazole sublimes on the sides of the vessel:

0.1504 gave 17.8 c.c. N_2 at 15° and 757 mm. $N = 13.8$.

0.1504 „ 18.4 c.c. N_2 „ 15° „ 757 mm. $N = 14.13$.

0.1488 „ 0.1090 $BaSO_4$. $S = 10.6$.

$C_{12}H_9O_3N_3S$ requires $N = 15.27$; $S = 11.63$ per cent.

INSTITUTE FOR ORGANIC CHEMISTRY,

TECHNISCHE HOCHSCHULE, DARMSTADT.

XIII.—The Absorption Spectra of Some Derivatives and Isomerides of 1:2-Diketo- Δ^3 -cyclopentene.

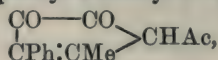
By JOHN EDWARD PURVIS.

THE author has already given an account of an investigation on the absorption spectra of some diketopyrroline compounds (Trans., 1910, **97**, 2535). The results showed that (1) the diketonic structure gives rise to the production of a well-marked colour and absorption; (2) the introduction of a methyl or a propyl group in an aromatic side-chain produces no fundamental change in the colour or the absorption; (3) the introduction of a methoxy- or a methylenedioxy-

group in an aromatic side-chain does not fundamentally alter the colour or the corresponding absorption, but another more refrangible band is produced characteristic of each type of radicle; (4) the replacement of oxygen in a ketonic group by the :N·NHPh group produces a change in the colour and the absorption, so that two bands are developed, the less refrangible one being the stronger; (5) the replacement of both oxygen atoms and the establishment of a phenazine ring is marked by a further change in the colour from red to yellow, a decrease in the strength of the less refrangible band, and an increase in the strength of the more refrangible one; (6) the increased weight of the molecule shifts the position of general absorption towards the more refrangible regions.

That there is an intimate connexion between the absorption and the ketonic constitution is further shown from a consideration of the following 1:2-diketo- Δ^3 -cyclopentene compounds described by Ruhemann and Merriman (Trans., 1905, **87**, 1383) and by Ruhemann (Trans., 1909, **95**, 984, 1603; 1910, **97**, 462, 1438). From chemical considerations, the authors ascribed the following constitutional formulæ to the various compounds:

1:2-Diketo-5-acetyl-3-phenyl-4-methyl- Δ^3 -cyclopentene,



red.

The corresponding oxime, $\begin{array}{c} \text{C}(\text{:NOH}) \cdot \text{CO} \\ | \qquad \qquad \qquad \diagup \\ \text{CPh} \text{=} \text{CMe} \end{array} \text{CHAc}$, orange-yellow.

The corresponding phenylhydrazone, $\begin{array}{c} \text{C}(\text{:N} \cdot \text{NHPh}) \cdot \text{CO} \\ | \qquad \qquad \qquad \diagup \\ \text{CPh} \text{=} \text{CMe} \end{array} \text{CHAc}$, yellow.

The sodium compound, $\begin{array}{c} \text{C}(\text{ONa}) \cdot \text{CO} \\ | \qquad \qquad \qquad \diagup \\ \text{CPh} \text{---} \text{CMe} \end{array} \text{CAc}$, blue.

The isophenazine derivative, $\begin{array}{c} \text{CPh} \text{=} \text{C} \cdot \text{NH} \\ | \qquad \qquad \diagup \\ \text{CMe} \cdot \text{CAc} \cdot \text{C} \text{=} \text{N} \end{array} \text{C}_6\text{H}_4$, raspberry-red.

Solutions of these substances in milligram-molecules by weight in cold absolute alcohol have been investigated in the usual way. For example, *N*/100-solution means that one milligram-molecule by weight of the substance was dissolved in 100 c.c. of cold absolute alcohol; a *N*/1000-solution means that one milligram-molecule by weight of the substance was dissolved in 1000 c.c. of cold absolute alcohol.

The red 1:2-diketo-5-acetyl-3-phenyl-4-methyl- Δ^3 -cyclopentene in *N*/100-alcoholic solution was examined through various thicknesses of the solution, ranging from 3 mm. to 45 mm., but no band was observed. The positions where general absorption began through

the following thicknesses expressed in Ångström's units and in oscillation frequencies were:

	λ	$\frac{1}{\lambda}$
3 mm. thickness	3850	2596
6 " "	3920	2550
9 " "	5000	1999
12 " "	5320	1879
30 " "	5450	1833
45 " "	5450	1833

The $N/100$ -solution was then diluted with absolute alcohol, so that 1000 c.c. contained one milligram-molecule by weight, or $N/1000$ -strength. This solution was examined, and a band became apparent through 2 mm. thickness. The positions where general absorption began through greater thicknesses are also noted in the following table:

2 mm. thickness band between λ 3250 and λ 2820				$\frac{1}{\lambda}$
			λ	
9 " "	general absorption began at	3490	2864	
30 " "	" " " "	3830	2609	

The $N/1000$ -alcoholic solution was then diluted with alcohol, so that the solution contained one milligram-molecule in 10,000 c.c. absolute alcohol, and on examining this $N/10,000$ -solution the band in the ultra-violet was better marked, and the absorption curve has been drawn (Fig. 1, I). The head of the band is at about 3325 (oscillation frequencies).

A $N/10,000$ -solution of the yellow-coloured oxime of diketoacetyl-phenylmethylcyclopentene was also examined, and it exhibited no band through the following thicknesses. The following numbers give the positions where general absorption began:

	λ	$\frac{1}{\lambda}$
2 mm. thickness	2180	4586
4 " "	2270	4403
10 " "	2520	3965
20 " "	2780	3595
30 " "	2890	3459

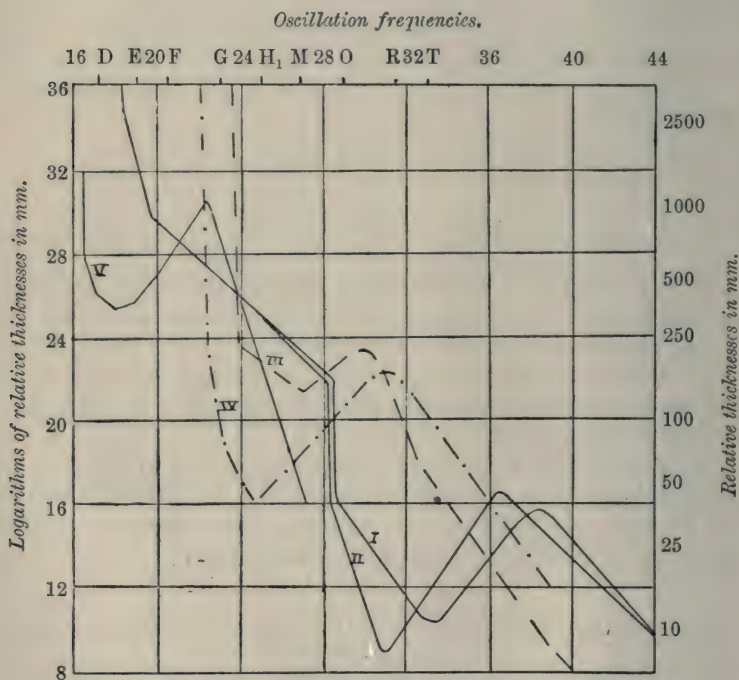
but on examining a $N/1000$ -solution of the oxime a strong band was exhibited, the absorption curve of which has been drawn, and the head of which is at about 2470 (oscillation frequencies) (Fig. 1, IV).

A $N/10,000$ -solution of the yellow phenylhydrazone of diketo-phenylmethylacetyl-cyclopentene was also examined, but no band was exhibited through the following thicknesses, and the numbers represent the positions where general absorption began:

	λ	$\frac{1}{\lambda}$
4 mm. thickness	2380	4199
8 " "	2590	3859
16 " "	2770	3608
24 " "	2850	3506
32 " "	3080	3246

On examining a *N*/1000-solution, however, a band was developed, the curve of which has been drawn (Fig. 1, III). The head of the

FIG. 1.



- I. Alcoholic solution of 1:2-diketo-5-acetyl-3-phenyl-4-methyl- Δ^3 -cyclopentene.
 II. " " the sodium compound of 1:2-diketo-5-acetyl-3-phenyl-4-methyl- Δ^3 -cyclopentene.
 III. " " " phenylhydrazone of " " " "
 IV. " " " oxime of " " " "
 V. Benzene solution of 5-acetyl-3-phenyl-4-methyl- Δ^3 -cyclopentene.

band is at about 2700 (oscillation frequencies). It may be mentioned here that hydroxylamine hydrochloride shows no bands in the ultra-violet (Hartley and Dobbie, *Trans.*, 1900, **77**, 318), and the author has shown that solutions of phenylhydrazine exhibit no bands (*Trans.*, 1910, **97**, 2540).

As exhibited from the above numbers, the red colour of the

1:2-diketocyclopentene compound is produced by a general absorption of the yellow, blue, green, and violet rays well in the visible spectrum, and only in the $N/10,000$ -solution is there a band apparent in the ultra-violet regions. In the red diketonic pyrroline before described (*loc. cit.*), there is a band which is between the regions of the visible and the invisible spectrum. The corresponding $N/10,000$ -solutions of the oxime and of the phenylhydrazone of the 1:2-diketocyclopentene compound do not show bands through equal thicknesses; but in each case a band is apparent in the less refrangible regions. The band of the heavier phenylhydrazone has a greater shift towards the more refrangible regions, and this phenomenon is comparable with similar phenomena observed in the diketopyrroline derivatives (*loc. cit.*).

The effect of sodium hydroxide on the 1:2-diketocyclopentene compound was shown by Ruhemann (*loc. cit.*) to change the colour from red to blue. In this blue compound, and in the isophenazine derivative, Ruhemann suggested that the positional linking of the ring is different from the others, and as indicated in the constitutional formulæ on p. 108. On examining and comparing the blue solution produced by adding one drop of sodium hydroxide to the red solution of the 1:2-diketocyclopentene compound, the change in colour was accompanied by the production of a narrower and more persistent band in the ultra-violet, and a greater shift towards the less refrangible regions (Fig. 1, II). Its head is at about 3080 (oscillation frequencies). A $N/100$ -solution of the blue-coloured solution was also examined, but no other band was observed, and the positions where general absorption began through the following thicknesses were:

3 mm. thickness	λ	$\frac{1}{\lambda}$
6	4020	2487
9	No rays were transmitted, for the panchromatic plates contained no images of any part of the spectrum.	
12		
15		
18		

That is to say, the blue colour was produced by a general absorption of the red and yellow rays, accompanied by a narrowing of the band in the ultra-violet.

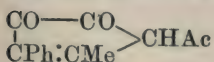
In the isophenazine raspberry-red derivative, where both the oxygen atoms in the ketonic groups are replaced, and where Ruhemann suggests a positional change in the valencies of the cyclopentene nucleus, a large band is exhibited in $N/1000$ -solution in benzene (the substance is insoluble in alcohol). The absorption curve of this band has been drawn (Fig. 1, V), and corresponds with the purple colour. Its head is at about 1800 (oscillation

frequencies). *N*/10,000-Solutions of the substance were also examined, but no other bands became apparent, and benzene itself through 2 mm. thickness absorbs the light beyond λ 3010. The positions where general absorption began in the *N*/10,000-solution in benzene were:

2 mm. thickness	λ	$\frac{1}{\lambda}$
10 " "	3010	3320
20 " "	3290	3038
20 " "	3580	2791
30 " "	3720	2687

It is important to compare the bands of the phenylhydrazone and the *isophenazine* derivative of the diketocyclopentene with the corresponding derivatives of the diketopyrroline (*loc. cit.*). In the latter substance there is a second more refrangible band produced which is absent in the former. It follows from this comparison that the absorption is conditioned, not only by the diketonic structure, but also by the type of ring in which the structure occurs. The diketonic structure means the production of a striking colour, and the colour and selective absorption are altered when the oxygen atoms are replaced in the ketonic radicles by oxime and phenylhydrazine radicles. The absorption is also modified in different directions of the spectral regions according to the type of nucleus and the substituted radicles, as well as by alterations in the positional valencies of the atoms of the ring.

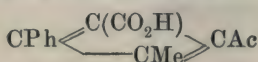
Other substances described by Ruhemann and Merriman (*loc. cit.*) have also been examined. The formulæ ascribed to these compounds from chemical considerations are:



1:2-Diketo-5-acetyl-3-phenyl-4-methyl- Δ^3 -cyclopentene, red.

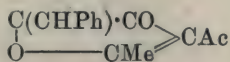
A.

(Described above.)



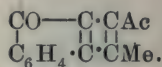
3-Acetyl-1-phenyl-4-methyl-1:3-cyclobutadiene-2-carboxylic acid, colourless.

B.



4-Keto-3-acetyl-5-benzylidene-2-methyl-dihydrofuran, light yellow.

C.



Indone - cyclo-methylaceto-ethylene, reddish-brown.

D.

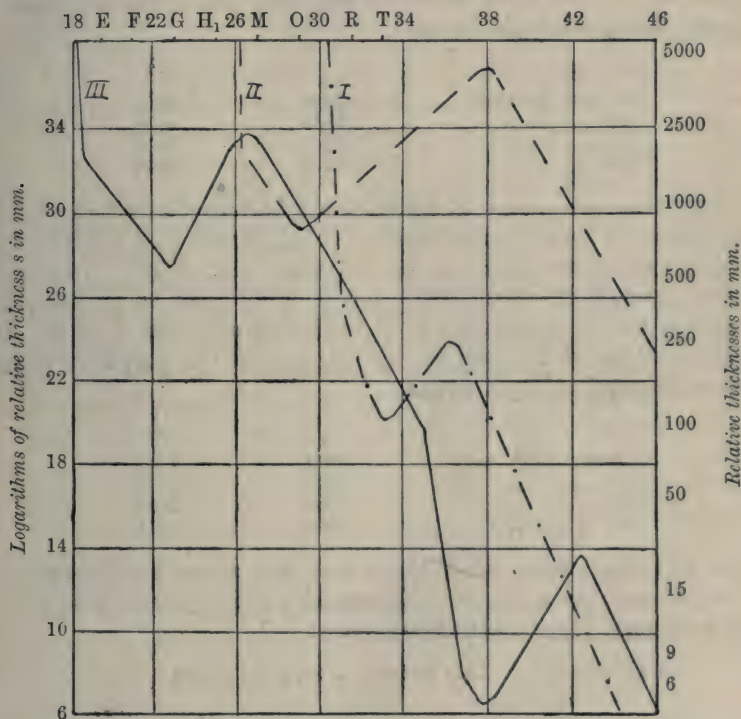
The substances A, B, and C are isomeric compounds. The absorption curve for A, the 1:2-diketo- Δ^3 -cyclopentene compound, has been already drawn (Fig. 1, I) and discussed in relation to its derivatives.

The colourless substance B, 3-acetyl-1-phenyl-4-methyl-1:3-cyclo-

butadiene-2-carboxylic acid, which does not possess a ketonic structure, was examined in various strengths of alcoholic solutions, and a $N/1000$ -solution exhibited a weak band in the ultra-violet, the curve of which has been drawn (Fig. 2, I). It is interesting to note that the position of this band, whose head is at 3300, coincides

FIG. 2.

Oscillation frequencies.



I. Alcoholic solution of 3-acetyl-1-phenyl-4-methyl-1:3-cyclobutadiene-2-carboxylic acid.

II. " " 4-keto-3-acetyl-5-benzylidene-2-methyldihydrofuran.

III. " " indone-cyclomethylacetoethylene.

with that found in the 1:2-diketocyclopentene compound itself, and it is possibly a benzenoid band (Fig. 1, I). $N/100$ -Solutions were also examined, and at 2 mm. thickness the band was observed between λ 3140 and λ 2820, and the positions where general absorption begins in $N/100$ -solution of the substance *B* are:

2 mm. thickness band between λ 3140 and λ 2820

				λ	$\frac{1}{\lambda}$
10	"	"	general absorption began	3280	3047
20	"	"	" " "	3320	3104
30	"	"	" " "	3330	3002
40	"	"	" " "	3345	2989
50	"	"	" " "	3350	2983
60	"	"	" " "	3360	2976

$N/10,000$ -Alcoholic solutions of the substance *B* were also examined, but no band was observed, and the positions where general absorption began were:

		λ	$\frac{1}{\lambda}$
2 mm. thickness		2190	4564
10 " "		2345	4263
20 " "		2500	3997
30 " "		2535	3943

The yellow compound *C*, 4-keto-3-acetyl-5-benzylidene-2-methylidihydrofuran, a ketonic substance, in $N/10,000$ -solution exhibited a band the curve of which has been drawn (Fig. 2, II). The head of the band is at about 2900, and it is different in position, in intensity, and in persistence from the bands of either *A* or *B*. In $N/100$ -solution of *C* there was no band, and the positions where general absorption began were:

		λ	$\frac{1}{\lambda}$
2 mm. thickness		2800	2631
10 " "		3940	2537
20 " "		4050	2468
30 " "		4039	2474

In $N/1000$ -solution of *C* there was the above band observed through 2 mm. thickness, and the positions where general absorption began through greater thicknesses were:

2 mm. thickness band between λ 3670 and λ 2900

			λ	$\frac{1}{\lambda}$	
10	"	"	general absorption begins at	3790	2637
30	"	"	" " " "	3650	2739

The reddish-brown substance *D*, indone *cyclomethylacetethylene*, a ketonic compound to which a double ring formula has been ascribed, exhibits two bands. A $N/100$ -solution shows a band the head of which is at about $1/\lambda$ 2260 (Fig. 2, III); and a $N/10,000$ -solution exhibits another band the head of which is at about $1/\lambda$ 3780. It is evident, therefore, that these two bands distinguish it from the substances *A*, *B*, and *C*, in that it has two bands whilst the others have one. The production of the two rings means the production of two absorption bands, the band

at 3780 corresponding with the ring $C_6H_4<$, and the band at 2260 corresponding with the ring $\begin{array}{c} -C:C- \\ | \quad | \\ -C:C- \end{array}$.

The colour of both the compounds *C* and *D*, like that of *A*, are produced by a general absorption of the rays well in the visible spectrum, *A* being red, *C* being light yellow, and *D* being reddish-brown.

General Conclusions.

It is clear from a comparison of these observations and of those of the 2:3-diketopyrrolines (*loc. cit.*) that (1) the colour is determined primarily by the presence of either a monoketonic or a diketonic structure; (2) the absorption in the more refrangible regions of the monoketonic compounds is further determined by the type of ring in which the ketonic structure occurs; (3) in the 1:2-diketonic cyclopentene compounds, the colour is modified in the direction of the more refrangible regions by the introduction of an oximo- or of a $:N \cdot NHP$ group, a result precisely analogous to that which has been previously observed in the 2:3-diketopyrrolines; (4) in the 1:2-diketonic cyclopentene compounds, the absorption in the ultra-violet of the phenylhydrazone or of the isophenazine derivative is wholly different from that of the corresponding substances derived from the 2:3-diketopyrrolines; and (5) the difference in the isophenazine compound may be explained partly as the result of an alteration in the positional valencies of the ring, as suggested by Ruhemann (*loc. cit.*). The explanation also applies to the blue sodium compound of the 1:2-diketocyclopentene. In the isophenazine compound, the absorption is not moved in the direction of the more refrangible rays like that which occurs in the phenazine obtained from the diketopyrroline. Further, as regards the blue sodium compound of the 1:2-diketocyclopentene, besides the change in colour from red to blue, the band in the ultra-violet becomes narrower and more persistent, and is shifted towards the more refrangible end of the spectrum.

My thanks are due to the Government Grant Committee of the Royal Society, by whose assistance the spectroscope was purchased, and to Dr. Ruhemann for specimens of the pure substances.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

XIV.—*Preparation of Ammonium Nitrite by the Sublimation in a Vacuum of a Mixture of Ammonium Chloride and Alkali Nitrites.*

By PAÑCHĀNAN NEOGI, M.A., and BIRENDRA BHUSAN ADHICĀRY, M.A.

RÂY (Trans., 1909, **95**, 345) has recently shown that solid ammonium nitrite sublimes in small quantities with decomposition when a dilute solution (0·7 to 2·0 per cent.) of the salt, obtained by the double decomposition of silver or barium nitrite and ammonium chloride or sulphate respectively, is gently heated in a vacuum. We have now found that the salt may be obtained in fairly large quantities by evaporating and subliming in a vacuum a very concentrated solution of a mixture of ammonium chloride and sodium or potassium nitrite.

EXPERIMENTAL.

The apparatus employed is as follows. A distilling flask of fairly large capacity is connected with a condenser, to the other end of which are attached two filtering flasks connected with each other by means of pressure tubing, and immersed in cold water. The first serves as a receiver, and the second, which contains a quantity of concentrated sulphuric acid, is connected with a manometer and a Geryk pump. The flask is heated in a water- or, better, paraffin-bath.

Twenty-three grams of ammonium chloride and 35 grams of sodium nitrite (or 42 grams of potassium nitrite) were dissolved in the minimum quantity of cold water, the solution transferred to the distilling flask, the latter connected with a condenser, and the Geryk pump set to work. The flask was immersed in a paraffin-bath up to the portion containing the solution, and the temperature of the bath was maintained between 50° and 60°. Water distilled with gentle frothing, but without bumping. Considerable bumping, however, takes place if a naked flame is used instead of a bath. The filtering flasks dipped in cold water arrested any escaping moisture, which would otherwise enter the pump and condense in the manometer. When a certain concentration was reached, minute bubbles of gas were evolved, and the mercury column descended slightly. The pump was worked from time to time to maintain the vacuum. Special care should be taken at the time when the mass just becomes solid. At this point the temperature should not be raised above 60°, and the pump should be constantly worked, as otherwise the whole of the nitrite would decompose with almost

explosive violence. When once the mass has solidified and become perfectly quiescent, the liability of the nitrite to decompose is almost removed. The temperature of the bath was then gradually raised to 80° , when the solid nitrite began to sublime.* The flask was gradually lowered into the bath as the sublimate rose higher and higher, until the whole mass was collected as a thick, circular crust at the top of the bulb of the flask. The bath was then removed, and air was admitted, not by opening the screw in the pump (as in that case the moist air would dissolve the whole quantity of the extremely hygroscopic nitrite formed), but by gently opening the cork of the flask. The bottom of the latter was then broken, and the solid mass quickly scraped off with a spatula. The substance was so very deliquescent that it was difficult to remove the whole quantity of the salt obtained. A considerable portion of the salt decomposed, and a part escaped into the condenser with the steam. The liquid collected in the receiver contained much ammonium nitrite as well as a small quantity of the chloride.

The liquid in the receiver was transferred to the distilling flask, and evaporated in a vacuum as before. A second crop of the nitrite sublimed, and was collected.

Analysis.

The substance obtained consists of fine flakes, and is extremely hygroscopic. It liberates iodine copiously when treated with potassium iodide solution acidified with dilute hydrochloric acid. When silver nitrate solution is added to the solution of the substance, a crystalline precipitate of silver nitrite is obtained, which dissolves in hot water, leaving in some cases a faint opalescence. That the substance does not contain any ammonium nitrate is shown by the fact that the amount of nitrogen yielded by the "urea" method is identical with that of the nitric oxide obtained by the Crum-Frankland method. The "ammonia" nitrogen in the salt, as estimated by the Nessler test, bears the ratio of 1:1 to the nitrogen in the acid radicle. The substance is therefore proved to be pure ammonium nitrite.

The salt may be kept undecomposed in an ordinary desiccator over concentrated sulphuric acid or in sealed tubes. If kept in a vacuum desiccator, the salt vaporises, and within two or three days the greater part is lost, and the odour of nitrous fumes, formed by the action of the sulphuric acid on the vaporised nitrite, is perceived on opening the desiccator.

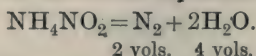
* It was found by blank experiments that solid ammonium chloride commenced to sublime in small quantities when the temperature of the bath was above 140° and the pressure was between 10 and 20 mm.

Ammonium nitrite volatilises in steam. A solution of the salt was placed in a distilling flask, and steam was admitted into it. The pump was worked, and after some time the distillate was tested, when appreciable quantities of ammonium nitrite were found in it.

We confirm Rây's observation (*loc. cit.*) that the re-sublimed salt does not explode on heating, although, as already pointed out, the salt sometimes decomposes with almost explosive violence as its concentrated solution just becomes solid.

Vapour Density of Ammonium Nitrite.

The question whether the sublimation of ammonium nitrite is really a case of sublimation or dissociation was left open by Rây (*loc. cit.*). In order to decide the point, we determined the vapour density of the salt according to Hofmann's method. Using chloroform vapour to heat the Hofmann tube, it was found that the solid substance was only partly vaporised, and with ethyl alcohol, also, it was found that some portion of the substance still remained solid. At 100°, using steam, the density of the resulting gas was found to be 12·7. This result shows that at 100° the salt almost entirely decomposes according to the usual equation:



The decomposition according to the above reaction, in which one molecular proportion of ammonium nitrite decomposes into two volumes of nitrogen and four volumes of water vapour, would give the vapour density of ammonium nitrite as 10·6, the density actually obtained being 12·7.

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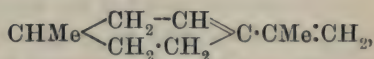
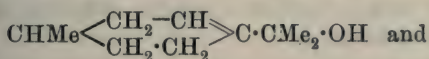
XV.—On dl- and d- Δ^2 -m-Menthenol(8) and dl- and d- $\Delta^{2:8(9)}$ -m-Menthadiene.

By WALTER NORMAN HAWORTH (1851 Exhibition Scholar of Manchester University), WILLIAM HENRY PERKIN, jun., and OTTO WALLACH.

In a paper published recently (Trans., 1910, 97, 1427), attention was directed to the difficulty of obtaining substances belonging to the terpene group, and especially the terpenes themselves, in a condition pure enough to allow of the accurate determination of their physical

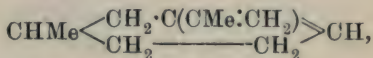
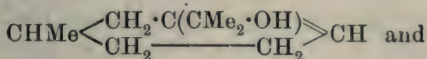
properties. In order that such substances may be characterised with the least probability of error, it was pointed out how desirable it was that they should, whenever possible, be prepared by two independent methods, so selected that there could be no doubt as to the constitution of the resulting product.

If, then, the two preparations of the substance are found to agree substantially in chemical and physical properties, it may be assumed that the values obtained correctly represent the characteristics of that substance. In the communication referred to, the substances studied were Δ^3 *p*-menthenol(8) and $\Delta^{3:8(9)}$ *p*-menthadiene,

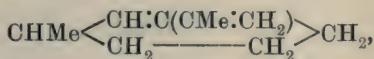
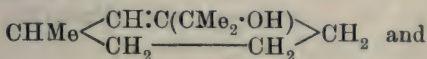


and the influence exerted by the proximity of the double linking to the group $>\text{CMe}_2 \cdot \text{OH}$ in the menthenol, and especially the high values resulting from the conjugated position of the double linkings in the case of the menthadiene, were discussed in some detail.

Shortly afterwards Luff and Perkin (Trans., 1910, 97, 2147; compare *ibid.*, 1905, 87, 1099) described a method by which Δ^3 -*m*-menthenol(8) and $\Delta^{3:8(9)}$ -*m*-menthadiene,



could be obtained in much larger quantity than had previously been possible, and although, so far, only this one method is available for the preparation of these substances, there can be little doubt that they were so pure that the determination of their physical and other properties may be accepted as accurate. The present communication deals with the characteristics of Δ^2 -*m*-menthenol(8) and $\Delta^{2:8(9)}$ -*m*-menthadiene,

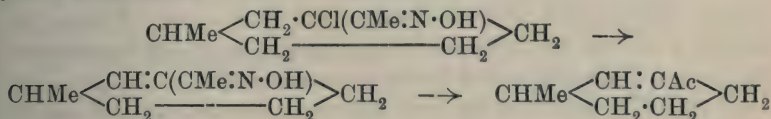


and the results are of special interest in view of the close relationship of these substances with the Δ^3 -isomerides just mentioned.

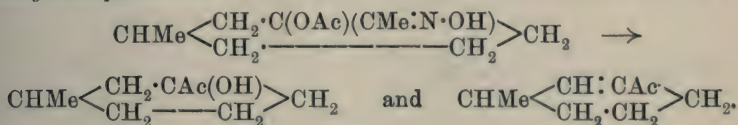
Δ^2 -*m*-Menthenol(8) and $\Delta^{2:8(9)}$ -*m*-menthadiene were first obtained in 1905 by Perkin and Tattersall (Trans., 87, 1101) from 1-methylcyclohexan-3-carboxylic acid (hexahydro-*m*-toluic acid).

This acid was first converted into 3-bromo-1-methylcyclohexan-3-

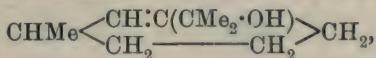
which is crystalline and melts at 68° . The nitroso-chloride of *l*-1-methyl-3-ethylidenecyclohexane reacts readily when boiled with sodium acetate in acetic acid solution, with elimination of hydrogen chloride and formation of the *oxime* of *d*-3-acetyl-1-methyl- Δ^2 -cyclohexene, which melts at 79° and, when hydrolysed with mineral acids, yields the ketone :



this distils at 212° and has $[\alpha]_D +100.4^\circ$, reversal of rotation having again taken place. The action of sodium acetate and acetic acid on the nitroso-chloride proceeds in another direction at 65° with separation of sodium chloride and formation of the *oxime* of 3-acetoxy-3-acetyl-1-methylcyclohexane, and this, when treated with dilute sulphuric acid, yields a mixture of 3-acetyl-1-methylcyclohexan-3-ol and 3-acetyl-1-methyl- Δ^2 -cyclohexene :

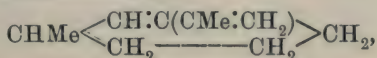


d-3-Acetyl-1-methyl- Δ^2 -cyclohexene reacts readily with magnesium methyl iodide, and the resulting *d*- Δ^2 -m-menthenol(8),

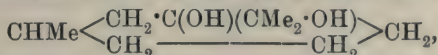


distils at $103\text{--}105^\circ/22$ mm., has $[\alpha]_D +55.6^\circ$, and yields a phenylurethane, which melts at 124° ; its constitution was controlled by oxidation with permanganate, when it was found to yield α -methyladipic acid.

This menthenol is readily decomposed by shaking with dilute sulphuric acid at the ordinary temperature, with loss of water and formation of *d*- Δ^2 -m-menthadiene,



which distils at $181^\circ/736$ mm., and has $[\alpha]_D +64.0^\circ$. The corresponding *terpin* (1-methyl-3- α -hydroxyisopropylcyclohexan-3-ol),



a crystalline substance which melts at 64° , was obtained from *d*-3-acetyl-1-methylcyclohexan-3-ol (p. 132) by treatment with the Grignard reagent.

Although prepared by such widely differing methods, it was interesting to find that the properties of *d*- Δ^2 -m-menthenol(8) and

d - $\Delta^{2,8(9)}$ - m -menthadiene approximate very closely to, if they do not actually coincide with, those of the corresponding dl -isomerides.

The careful consideration of the experimental results described in this communication shows that they confirm and amplify certain deductions as to the general behaviour and properties of menthenols and menthadienes which were discussed in some detail on a previous occasion (Perkin and Wallach, *Trans.*, 1910, **97**, 1427). A complete discussion of this interesting subject would take up too much space, but the following points may be briefly emphasised.

Δ^2 - and Δ^3 - m -Menthenol(8) and Δ^3 - p -menthenol(8) all contain the grouping $\geq C \cdot CMe_2 \cdot OH$, that is to say, they contain an ethenoid linking in direct conjunction with the $\cdot CMe_2 \cdot OH$ group, and the influence of this conjunction may be gathered from the following summary of the more important physical and chemical properties of the (dl -) substances:





- I. Δ^3 - p -Menthenol(8), Me  $CM_e_2 \cdot OH$.
- II. Δ^2 - m -Menthenol(8), Me  $CM_e_2 \cdot OH$.
- III. Δ^3 - m -Menthenol(8), Me  $CM_e_2 \cdot OH$.
- IV. Δ^1 - p -Menthenol(8), Me  $CM_e_2 \cdot OH$.
- (Terpineol.)

TABLE I.

	I.	II.	III.	IV.
B. p.	205°	110°/30 mm.	102°/14 mm.	124°/30 mm.
M. p.	39	—	—	35°
d 20/20°	0.921	0.9281	0.9268	0.938
n_D	1.4764	1.4772	1.4798	1.4820
M (calc. 47.16)	47.2	46.9	47.10	46.8
M. p. of phenylurethane*	128°	127°	130°	113°

* The phenylurethanes have been added in order to make the table more valuable for purposes of identification.

It is evident from this table that the approach of the ethenoid linking to the $\cdot CMe_2 \cdot OH$ group, whilst it has a tendency to cause a fall in boiling point, density, and refractive index, does not produce any very striking effect on the physical properties of the substance.

When, however, the properties of the corresponding menthadienes are tabulated, it is at once obvious that the effect of the conjugated group $\geq C \cdot CMe \cdot CH_2$, or, in other words, the effect of the approach of the ethenoid linking to the $\cdot CMe \cdot CH_2$ group, is very marked.

The numbers in table II refer to the following substances :

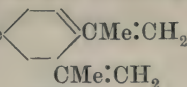
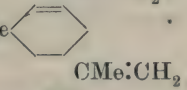
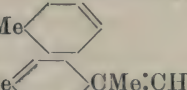
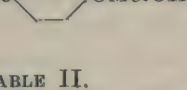
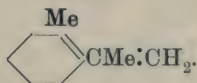
- I. $\Delta^{3:8(9)}$ -*p*-Menthadiene, 
 II. $\Delta^{2:8(9)}$ -*m*-Menthadiene, 
 III. $\Delta^{3:8(9)}$ -*m*-Menthadiene, 
 IV. $\Delta^{1:8(9)}$ -*p*-Menthadiene, 
 (Limonene)

TABLE II.

	I.	II.	III.	IV.
B. p.	185°	182°	182°	176°
<i>d</i> 20/20°	0.858	0.8624	0.8609	0.846
<i>n</i> _D	1.4924	1.5030	1.4975	1.4746
M	46.0	46.6	46.3	45.2
(Calc. $ \epsilon ^2 =$	45.24)			

The consideration of these figures brings out very clearly the fact that, in the cases I, II, and III, which are now available for comparison, the effect of conjugation is to raise boiling point, density, and especially refractive index to a remarkable degree above the corresponding values of limonene (IV), but the position of the methyl group in relation to the group $\text{>C}\cdot\text{CMe}\cdot\text{CH}_2$ does not appear to have any distinct effect on these values.

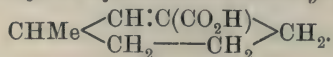
It has been repeatedly pointed out (compare Trans., 1905, 87, 641) that menthadienes containing conjugated ethenoid linkings have also well characterised chemical properties; they are, for example, only capable of combining with two atoms of bromine or one molecule of hydrogen chloride, whereas others, for example, limonene and carvestrene, in which the ethenoid linkings are not conjugated, yield additive compounds with four atoms of bromine and two molecules of hydrogen chloride. The effect of conjugation in the case of an *o*-menthadiene, $\Delta^{1:8(9)}$ -*o*-menthadiene,



for example, on physical properties has still to be investigated, but, since it has already been observed (Trans., 1905, 87, 1077) that this terpene is only capable of combining with two atoms of bromine, it is highly probable that, in physical properties also, it will exhibit a similar behaviour to that of the conjugated *m*- and *p*-menthadienes (I, II, and III) which have just been discussed.

EXPERIMENTAL.

dl-1-Methyl- Δ^2 -cyclohexene-3-carboxylic Acid,



The 1-methylcyclohexan-3-carboxylic acid required for these experiments was prepared essentially according to the method already described (Perkin and Tattersall, *Trans.*, 1905, 87, 1091), and then converted into 3-bromo-1-methylcyclohexan-3-carboxylic acid in the following manner. The pure acid (50 grams) was treated with phosphorus pentachloride (76 grams), at first at the ordinary temperature and then on the water-bath, and when conversion into the acid chloride was complete, bromine (60 grams) was added and the whole heated in a reflux apparatus on the water-bath for ten hours.

The product was poured in a thin stream into alcohol (250 c.c.), and, after twenty-four hours, water was added, the bromo-ester extracted with ether, the ethereal solution well washed, very carefully dried, and evaporated.

In order to convert the bromo-ester into the mixed esters of 1-methyl- Δ^2 - and 1-methyl- Δ^3 -cyclohexene-3-carboxylic acids, it was heated, in quantities of 30 grams, with five times its volume of diethylaniline in a reflux apparatus to boiling for five hours.

Sufficient dilute hydrochloric acid was then added to dissolve the diethylaniline, the ester extracted with ether, the ethereal solution washed with sodium carbonate, evaporated, and the residue fractionated, when almost the whole quantity passed over at 145—150°/100 mm.

This was hydrolysed with excess of methyl-alcoholic potassium hydroxide on the water-bath, water was then added, the alcohol removed by evaporation, the acid precipitated by hydrochloric acid, extracted with ether, and distilled in steam. The steam distillate was boiled with excess of freshly precipitated calcium carbonate, filtered. the filtrate evaporated until long hairs began to separate, and then allowed to cool. The characteristic voluminous calcium salt was collected, together with further crops of the same salt obtained by concentrating the mother liquor. It was mentioned in the previous communication (*loc. cit.*, p. 1096) that it is not easy to recrystallise this salt in the usual manner, and to get over this difficulty, the acid was regenerated from the salt by hydrochloric acid, distilled in steam, and again converted into the calcium salt, in order to remove any traces of the Δ^3 -acid; this treatment was repeated three times. Lastly, the pure salt was decomposed, the acid extracted with ether, and distilled, when it boiled constantly at 150°/11 mm., and when cooled in a freezing mixture showed no signs of crystallising.

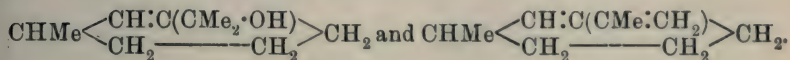
On the first occasion (*loc. cit.*, p. 1096) a small quantity of the pure Δ^3 -acid was isolated from the mother liquors of the calcium salt of the Δ^2 -acid, but, under the conditions described above, hardly any of this acid appears to be produced. The separation of the Δ^2 - and Δ^3 -isomerides, which seems to be complete, was at first thought to depend on difference in solubility of the calcium salts; that this is not the only reason, and that the separation depends also on the fact that the salt of the Δ^2 -acid is present in much the larger quantity than that of the Δ^3 -isomeride, seems to be very probable. In order to test this point, the calcium salt of 1-methyl- Δ^3 -cyclohexene-3-carboxylic acid (m. p. 58—60°; compare *Trans.*, 1910, **97**, 2151) was prepared by boiling the acid with water and calcium carbonate. On concentrating the solution, the calcium salt separated in needles and had a somewhat similar appearance to the calcium salt of the Δ^2 -acid, and there did not appear to be any striking difference in the relative solubilities of the two salts. The calcium salt of the Δ^3 -acid was collected, washed, and left on porous porcelain exposed to the air for ten days; it then yielded on analysis numbers which agree approximately with those required by the formula $(C_8H_{11}O_2)_2Ca, 5H_2O$:

1.0038, dried at 130° until constant, lost 0.2149 and yielded 0.3375

$CaSO_4$. $Ca = 9.8$; $H_2O = 21.4$.

$(C_8H_{11}O_2)_2Ca, 5H_2O$ requires $Ca = 9.8$; $H_2O = 22.1$ per cent.

dl- Δ^2 -m-Menthenol(8) and dl- $\Delta^{2:8(9)}$ -m-Menthadiene,



The following conditions give a more satisfactory yield of Δ^2 -m-menthenol(8) than those originally employed (*Trans.*, 1905, **87**, 1099). Ethyl 1-methyl- Δ^2 -cyclohexene-3-carboxylate (20 grams) is added to an ethereal solution of magnesium methyl iodide (containing 10 grams of magnesium), the solution allowed to remain for two days, then mixed with water, and distilled in steam. The distillate is extracted with ether, the ethereal solution dried over anhydrous sodium sulphate, evaporated, and the residue distilled under diminished pressure:

0.1277 gave 0.3643 CO_2 and 0.1349 H_2O . $C = 77.8$; $H = 11.8$.

$C_{10}H_{18}O$ requires $C = 77.9$; $H = 11.7$ per cent.

dl- Δ^2 -m-Menthenol(8) distils at 110°/30 mm., and is a rather viscid, colourless oil, which possesses in a marked degree the pleasant odour of terpineol and menthol characteristic of substances of this class. The determination of its physical properties gave: $d_{20/20^\circ} = 0.9281$, $n_D = 1.4772$, $M = 46.9$ (calc. 47.16), and it will be observed that

these correspond closely with the values found in the case of *d*- Δ^2 -*m*-menthenol(8) (compare p. 130).

The *phenylurethane* is readily obtained by mixing the menthenol with the calculated quantity of phenyl carbimide and leaving for several days; the crystalline mass was drained on porous porcelain and crystallised from dilute methyl alcohol:

0.1016 gave 4.7 c.c. N_2 at 18° and 755 mm. $N = 5.3$.

$C_{17}H_{23}O_2N$ requires $N = 5.1$ per cent.

This *phenylurethane* separates from methyl alcohol as a felted mass of long needles, and, when quickly heated, melts and decomposes at 127° . That it has the same constitution as the phenylurethane of *d*- Δ^2 -*m*-menthenol(8) is shown by the fact that the mixture of both melts at the same temperature as the constituents.

dl- $\Delta^{2:8(9)}$ -*m*-Menthadiene.—This terpene is readily obtained by digesting Δ^2 -*m*-menthenol(8) with 6 per cent. oxalic acid in a reflux apparatus for six hours, and then distilling in steam. The distillate was extracted with ether, the ethereal solution dried, evaporated, and the terpene distilled three times over sodium:

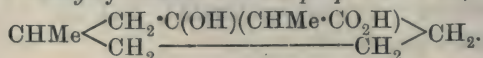
0.1061 gave 0.3425 CO_2 and 0.1140 H_2O . $C = 88.0$; $H = 11.9$.

$C_{10}H_{16}$ requires $C = 88.2$; $H = 11.8$ per cent.

dl- $\Delta^{2:8(9)}$ -*m*-Menthadiene distils at $182\text{--}183^\circ/770$ mm., and possesses a very pungent odour of lemons, quite distinct, however, from that of limonene; it gives an intense methylene-blue coloration when a drop of sulphuric acid is added to its solution in acetic anhydride.

The determination of the usual physical properties gave: $d_{20/20^\circ} = 0.8624$, $n_D = 1.5030$, $M = 46.6$ (calc. 45.24), and it will be seen that these agree closely with the values observed in the case of *d*- $\Delta^{2:8(9)}$ -*m*-menthadiene (p. 131). It had already been shown (*loc. cit.*, p. 1101) that the *dl*-terpene is only capable of combining with two atoms of bromine, and we have now found that it yields an additive derivative with only 1 molecule of hydrogen chloride.

1-Methylcyclohexan-3-ol-3-*a*-propionic Acid,



The ester of this acid was first prepared by Wallach and Evans (*Annalen*, 1908, 360, 51) from *d*-1-methylcyclohexan-3-one (from pulegone) by condensation with ethyl bromoacetate and zinc. In order to obtain the ester as pure as possible, the ketone was converted into the semicarbazone and this decomposed by mixing with dilute sulphuric acid and distilling in steam. During the hydrolysis of the ester by methyl-alcoholic potassium hydroxide, some decomposition

with regeneration of a small quantity of the ketone was observed, and this was removed by the addition of water and extraction with ether. The alkaline solution was acidified with dilute sulphuric acid, extracted with ether, the ethereal solution well washed, dried, and evaporated, and the residue left for a fortnight to crystallise. The crystals of 1-methylcyclohexan-3-ol-3- α -propionic acid after draining on porous porcelain, melted not quite sharply at 65°, but, as the acid is very readily soluble in the usual organic solvents and consequently difficult to recrystallise, it was used in this condition in all the subsequent experiments.

The analysis of the *silver* salt yielded the following result :

0.1905 gave 0.0637 Ag. Ag = 33.4.

$C_{10}H_{17}O_3Ag$ requires Ag = 33.3 per cent.

1-1-Methyl-3-ethylidenecyclohexane, $CHMe \begin{matrix} \text{CH}_2 \cdot C(\cdot CHMe) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{matrix} CH_2$.

When 1-methylcyclohexan-3-ol-3- α -propionic acid is heated under the ordinary pressure and in an atmosphere of hydrogen, it is readily decomposed with elimination of water and carbon dioxide, and the above hydrocarbon distils over. The crude product is mixed with a little sodium hydroxide and distilled in steam,* the distillate is extracted with ether, and the hydrocarbon distilled several times over sodium. 1-1-Methyl-3-ethylidenecyclohexane has the following physical properties : b. p. 152°, $d_{19/19}$ 0.8135, n_D 1.4590, M 41.67 (calc. 41.04), $[\alpha]_D - 50^\circ$.

The *nitroso-chloride*.—This derivative is prepared by mixing the hydrocarbon (10 c.c.) with glacial acetic acid (10 c.c.) and ethyl nitrite (10 c.c.), and adding from a dropping funnel, concentrated hydrochloric acid (5 c.c.) and glacial acetic acid (10 c.c.). After keeping for an hour, the nitroso-chloride is collected, washed with dilute alcohol or ether, left in contact with porous porcelain until dry, and then crystallised from acetone, from which it separates in colourless prisms, melting at 114°;

0.1200 gave 0.0916 AgCl. Cl = 18.9.

$C_9H_{16}ONCl$ requires Cl = 18.7.

The *nitrolpiperidide*, prepared from the nitroso-chloride by the action of piperidine, separates from methyl alcohol in colourless needles, and melts at 101—102°:

0.1016 gave 11.0 c.c. N_2 at 21° and 744 mm. N = 12.0.

$C_{14}H_{26}ON_2$ requires N = 11.8 per cent.

* The alkaline residue, on acidifying and extracting with ether, yields a mixture of unchanged hydroxy-acid and unsaturated acid, which may be employed in a subsequent preparation of the hydrocarbon.

Oxidation of 1-1-Methyl-3-ethylidenecyclohexane to 1-methyl-3-α-hydroxyethylcyclohexan-3-ol.—In carrying out this oxidation, the pure hydrocarbon (5 grams) was mixed with ice and mechanically shaken with a 1 per cent. solution of permanganate (12·7 grams KMnO_4). When the product was distilled in steam, a small quantity of unchanged hydrocarbon passed over, but no trace of 1-methylcyclohexan-3-one could be detected, the absence of this ketone being probably due to the fact that it is more readily oxidised than the hydrocarbon. The filtrate and washings of the manganese precipitate were evaporated to a small bulk, extracted with chloroform,* the chloroform extract dried over potassium carbonate and evaporated, when a syrup remained which soon crystallised. After contact with porous porcelain, the substance was crystallised from water or light petroleum, and thus obtained in colourless, silky needles, melting at 68° :

0·0918 gave 0·2288 CO_2 and 0·0928 H_2O . $\text{C} = 68\cdot0$; $\text{H} = 11\cdot2$.

$\text{C}_9\text{H}_{18}\text{O}_2$ requires $\text{C} = 68\cdot3$; $\text{H} = 11\cdot3$ per cent.

When this glycol is digested with dilute sulphuric acid, it yields a ketone which appears to be 3-acetyl-1-methyl- Δ^2 -cyclohexene.



The oxime of this ketone is produced when the nitroso-chloride of 1-1-methyl-3-ethylidenecyclohexane (10 grams) is mixed with anhydrous sodium acetate (10 grams) and glacial acetic acid (40 c.c.) and gently warmed with a small flame, and afterwards boiled for about ten minutes, during which, sodium chloride separates. The product is cooled, diluted with water, made alkaline with ammonia, and the crude oxime, which separates as a brown oil, extracted with ether. The ethereal solution is dried, evaporated, and the residue distilled under diminished pressure, when a colourless oil passes over at $140\text{--}150^\circ/20$ mm., which crystallises. After draining on porous porcelain, the oxime separated from ether or methyl alcohol in prisms melting at 79° :

0·0672 gave 5·7 c.c. N_2 at 22° and 741 mm. $\text{N} = 9\cdot3$.

$\text{C}_9\text{H}_{15}\text{ON}$ requires $\text{N} = 9\cdot2$ per cent.

The benzoyl derivative was obtained by adding benzoyl chloride to the solution of the oxime in dilute sodium hydroxide, and crystallises from methyl alcohol in long needles melting at $85\text{--}86^\circ$:

0·1095 gave 5·7 c.c. N_2 at 21° and 751 mm. $\text{N} = 5\cdot6$.

$\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{N} = 5\cdot4$ per cent.

* The aqueous solution yields, on acidifying and extracting with ether, a mixture of methyladipic acids.

d-3-Acetyl-1-methyl- Δ^2 -cyclohexene is obtained from the crude oxime by mixing with dilute sulphuric acid and distilling in steam.

The distillate is extracted with ether, the ethereal solution evaporated, and the crude ketone purified by conversion into the semicarbazone by means of semicarbazide hydrochloride and sodium acetate in the usual way. The crystalline mass thus obtained is a mixture of two semicarbazones, and is separated into its constituents by fractional crystallisation from alcohol. The less soluble constituent is the semicarbazone of d-3-acetyl-1-methyl- Δ^2 -cyclohexene and melts at 219°:

0.1046 gave 0.2365 CO₂ and 0.0822 H₂O. C = 61.6; H = 8.7.

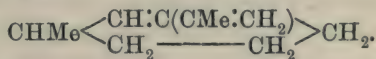
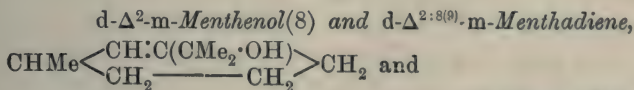
C₁₀H₁₇ON₃ requires C = 61.5; H = 8.7 per cent.

The more readily soluble constituent is the semicarbazone of 3-acetyl-1-methylcyclohexan-3-ol (m. p. 119°, p. 131). The semicarbazone of melting point 219° is decomposed with dilute sulphuric acid, and the ketone distilled in steam, extracted with ether, and fractionated under the ordinary pressure, when it boils constantly at 210—212°, and has an odour resembling that of menthone and cyclohexanone:

0.1334 gave 0.3821 CO₂ and 0.1252 H₂O. C = 78.1; H = 10.4.

C₉H₁₄O requires C = 78.2; H = 10.1 per cent.

The physical properties of this ketone are as follows: b. p. 210—212°, *d* 22/22° 0.9413, *n*_D 1.4817, *M* 41.77, [α]_D +100.4°, and it is interesting to compare these values with the corresponding properties of 4-acetyl-1-methyl- Δ^1 -cyclohexene and 4-acetyl-1-methyl- Δ^3 -cyclohexene, the properties of which have been tabulated in a previous paper (Trans., 1910, 97, 1432). It will also be observed that the rotation (−50°) of *l*-1-methyl-3-ethylidenecyclohexane has become dextro (+100.4°) during the conversion into the ketone.



In order to prepare the former of these substances, pure 3-acetyl-1-methylcyclohexene was added to an excess of an ethereal solution of magnesium methyl iodide, and, after keeping for one hour and heating on the water-bath for one hour, the product was decomposed by water and distilled in steam. The distillate was extracted with ether, the ethereal solution dried over potassium carbonate, evaporated, and the colourless residue distilled under diminished pressure:

0.0956 gave 0.2730 CO₂ and 0.1017 H₂O. C = 77.9; H = 11.8.

C₁₀H₁₈O requires C = 77.9; H = 11.7 per cent.

The physical properties of *d*- Δ^2 -*m*-menthenol(8) are the following: b.p. 206—208°/760 mm. or 103—105°/22 mm., *d* 22/22° 0.923, *n*_D 1.4728, *M* 47.21 (calc. 47.16), $[\alpha]_D +55.56^\circ$. The *phenylurethane*, prepared in the usual manner, separated from methyl alcohol in long, colourless needles, and melted at 124°. A comparison of these properties with those of *dl*- Δ^2 -*m*-menthenol(8) (p. 125) shows that, although the values are not identical, they correspond very closely.

Oxidation of d- Δ^2 -*m*-Menthenol(8) to α -Methyladipic Acid.

In investigating this degradation, the menthenol (1.5 grams) was oxidised with a 2 per cent. solution of permanganate (4.2 grams) at 0°, and then any unchanged menthenol removed by distillation in steam. The filtrate and washings of the manganese precipitate were concentrated and extracted with ethyl acetate, but only traces of a neutral substance (glycol) were left on evaporation. The alkaline solution was acidified, several times extracted with ether, the ethereal solution dried and evaporated, when a solid acid remained, which proved to be very difficult to crystallise. It was dissolved in dry ether and saturated with ammonia, when a crystalline salt separated, and by the addition of copper sulphate, this was converted into the blue copper salt, which was collected, washed, and dissolved in dilute hydrochloric acid. After removing the copper by hydrogen sulphide, the filtrate was evaporated, and the concentrated solution kept over solid potassium hydroxide in a vacuum desiccator, when a solid acid remained, which separated from a mixture of benzene and light petroleum as a crystalline powder, melting at 65—66°. The *silver* salt was analysed:

0.0370 gave 0.0212 Ag. Ag = 57.3.

$C_7H_{10}O_4Ag_2$ requires Ag = 57.7 per cent.

There can be no doubt that this acid is α -methyladipic acid, which Bone and Perkin (Trans., 1895, 67, 115) found to melt at 64°.

d- $\Delta^{2:8(9)}$ -*m*-Menthadiene.—This terpene is readily obtained when *d*- Δ^2 -*m*-menthenol(8), in quantities of 5 grams, is shaken mechanically with 500 c.c. of 1.5 per cent. sulphuric acid for a week, and the product neutralised with sodium carbonate and distilled in steam.*

The distillate is extracted with ether, the ethereal solution carefully dried, evaporated, and the hydrocarbon distilled several times over sodium, when it boiled constantly at 181°/736 mm., and had an odour different from that of limonene, but somewhat resembling that of sylvestrene. The analysis and determination of the usual physical

* The residue in the steam distillation flask was concentrated and several times extracted with ethyl acetate without, however, yielding a trace of the terpin.

constants gave the following results (compare the corresponding values of *dl*- $\Delta^{2:8(9)}$ -*m*-menthadiene, p. 126):

0.0953 gave 0.3084 CO₂ and 0.1028 H₂O. C = 88.2; H = 12.0.

C₁₀H₁₆ requires C = 88.2; H = 11.8 per cent.

d 17/17° 0.864, *n*_D 1.4946, M 45.87 (calc. 45.24), [α]_D + 64.0°.

The solution of the terpene in acetic anhydride gives, on the addition of sulphuric acid, an intense blue-violet coloration, which gradually changes to red.

The *dihydrochloride* of *d*- $\Delta^{2:8(9)}$ -*m*-menthadiene is obtained when *d*- Δ^2 -*m*-menthenol(8), dissolved in three times its volume of glacial acetic acid, is cooled in a freezing mixture and saturated with hydrogen chloride. On keeping, an oil separates at the surface, and, after adding ice, the heavy oil is extracted with ether, the ethereal solution washed with sodium carbonate, dried, evaporated, and the residue distilled under diminished pressure, when it passes over at 110–115°/12 mm., slight loss of hydrogen chloride taking place during the distillation:

0.1582 gave 0.1930 AgCl. Cl = 30.2.

C₁₀H₁₈Cl₂ requires Cl = 34.0 per cent.

d-3-Acetyl-1-methylcyclohexan-3-ol, CHMe $\left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CAc}(\text{OH}) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} \right\rangle \text{CH}_2$,

and *d*-1-Methyl-3- α -hydroxyisopropylcyclohexan-3-ol,

CHMe $\left\langle \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{OH})(\text{CMe}_2 \cdot \text{OH}) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} \right\rangle \text{CH}_2$.

It has already been stated (p. 128) that the nitroso-chloride of *l*-1-methyl-3-ethylidenecyclohexene is decomposed by boiling with sodium acetate and acetic acid for a few minutes with formation of the oxime of 3-acetyl-1-methyl- Δ^2 -cyclohexene. If, instead of boiling, the mixture is kept at 65° for fifteen minutes, the reaction proceeds somewhat differently, and, beside the above oxime, there is formed as the principal product the acetyl derivative of the oxime of 3-acetyl-1-methylcyclohexene-3-ol, which is a viscid gum. This was hydrolysed by treatment with dilute sulphuric acid (2 per cent.) and distillation in steam, and the distillate yielded, on extraction with ether, an oil which was converted into the mixed semicarbazones of melting points 199° and 219° by treatment with sodium acetate and semicarbazide hydrochloride (p. 129). These were separated by fractional crystallisation from alcohol, and the *semicarbazone* of *d*-3-acetyl-1-methylcyclohexan-3-ol (m. p. 199°) was analysed:

0.0938 gave 0.1946 CO₂ and 0.0768 H₂O. C = 56.5; H = 9.0.

C₁₀H₁₉O₂N₃ requires C = 56.3; H = 8.9 per cent.

The hydroxy-ketone is obtained from this semicarbazone by treat-

ment with dilute sulphuric acid, and is readily decomposed by boiling with dilute acids with elimination of water and formation of 3-acetyl-1-methyl- Δ^2 -cyclohexene (p. 128).

d-1-Methyl-3- α -hydroxyisopropylcyclohexan-3-ol is obtained when 3-acetyl-1-methylcyclohexan-3-ol is treated with magnesium methyl iodide, but it is most conveniently prepared by treating the mixture of ketones, obtained as explained on p. 129, with this reagent.

When the product is fractionated under diminished pressure, *d*- Δ^2 -*m*-menthenol(8) passes over first, and then a considerable quantity of a syrup distils at about 140°/23 mm., and, on cooling, solidifies.

This substance was left in contact with porous porcelain until quite free from oil, and then crystallised from light petroleum:

0.1063 gave 0.2721 CO₂ and 0.1130 H₂O. C = 69.8; H = 11.8.

C₁₀H₂₀O₂ requires C = 69.8; H = 11.6 per cent.

d-1-Methyl-3- α -hydroxyisopropylcyclohexan-3-ol melts at 64°, is readily soluble in water, and is an interesting substance, because it is the terpin corresponding with *d*- $\Delta^{2:8(6)}$ -*m*-menthadiene.

THE UNIVERSITIES OF GÖTTINGEN AND MANCHESTER.

XVI.—*The Direct Action of Radium on Ammonia.*

By EDGAR PHILIP PERMAN.

EXPERIMENTS have been made by Ramsay (Trans., 1908, **93**, 966), and more recently by Usher (Trans., 1910, **97**, 389), on the decomposition of ammonia by radium emanation. I have now tried the effect of the direct action of radium bromide, as it seemed possible that such experiments might facilitate the interpretation of the results obtained with the emanation. The apparatus employed consisted of two cylindrical bulbs, *A*, *B*, each of about 50 c.c. capacity, connected by capillary tubing, and a gauge tube, *C*, of 5 mm. diameter. Five milligrams of pure radium bromide were placed in a glass capsule at the lower end of *A*. The whole apparatus was then filled with ammonia through one of the side tubes, *D*, *E*, by repeated exhaustion and admission of ammonia. Mercury was introduced into the gauge, and the side tube sealed off, leaving the gas in each bulb under the atmospheric pressure. The bulbs were maintained at the same temperature by placing them in a dish of water, the gauge alone projecting. A mirror scale was fixed behind the gauge, and readings were taken every few days. At first the pressure in *A* decreased, as found by Ramsay with the emanation;

FIG. 1.

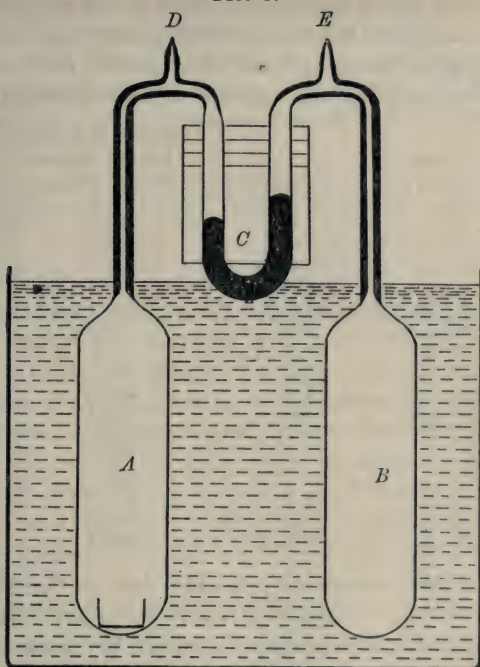
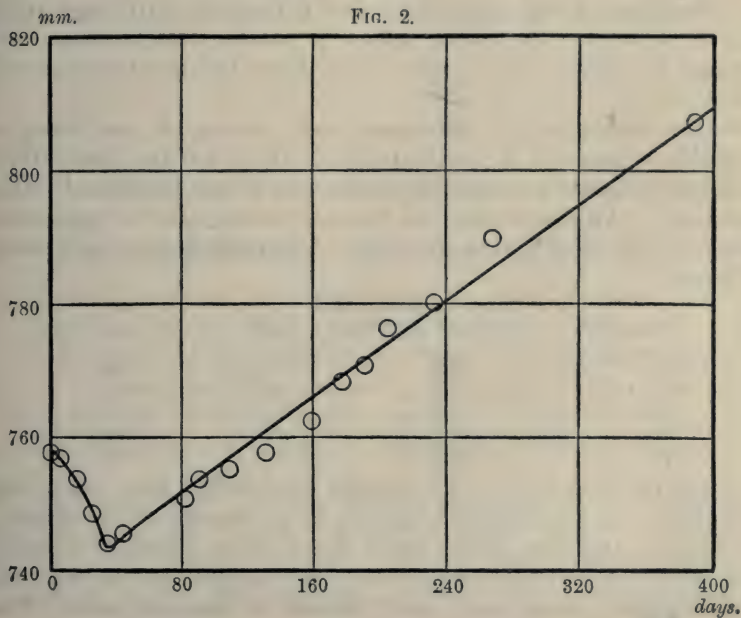


FIG. 2.



this continued for about five weeks, when a steady increase began. The pressures are given in the following table; they are calculated from the readings of the gauge, and the volumes of the bulbs *A*, *B*, corrections being made for the volumes of the connecting tubes:

Time.	Δp .	Pressure in bulb containing radium.
0 days	0.0 mm.	757.7 mm.
6 "	-0.5 "	756.9 "
16 "	-2.5 "	753.7 "
25 "	-5.6 "	748.5 "
35 "	-8.7 "	743.9 "
44 "	-7.6 "	745.4 "
82 "	-4.3 "	750.7 "
91 "	-2.5 "	753.7 "
109 "	-1.6 "	755.2 "
131 "	0.0 "	757.7 "
145 "	+1.5 "	760.1 "
159 "	2.9 "	762.4 "
177 "	6.7 "	768.3 "
191 "	8.3 "	770.8 "
205 "	11.7 "	776.3 "
233 "	14.2 "	780.3 "
268 "	20.2 "	789.9 "
389 "	30.9 "	807.2 "

The first fall of pressure is probably due to the presence of a small quantity of air. Supposing this to be present, the radiations from the radium would decompose some of the ammonia, and the hydrogen would form water with the oxygen of the air. When once the pressure has begun to increase, it increases fairly regularly. This is shown by the curve, which is nearly straight after the increase has begun. It is constructed from the numbers already given.

Before attempting to interpret these results, it was thought advisable to measure, if possible, whether there was any diminution of pressure caused by the gases being driven into the glass by the radiations. An experiment was therefore made with the apparatus as before, but filled with undried air. The following numbers were obtained:

Time.	Fall of pressure in bulb containing radium.	Δp .	$\frac{\Delta p}{\Delta t}$.
0 days.	0.0 mm.	—	—
20 "	2.0 "	2 mm.	0.10
31 "	3.9 "	1.9 "	0.17
49 "	6.5 "	2.6 "	0.14
92 "	13.2 "	6.7 "	0.16
116 "	16.7 "	3.5 "	0.15

After the first few days a regular contraction took place, and this showed no sign of falling off even in the course of four months. On opening the tube, it was found that a small globule of mercury had fallen into the capsule containing the radium, and on the sides of the capsule there was a small deposit of mercuric oxide. The

radiations thus caused the oxidation of mercury in the presence of moist air. As it was uncertain what part of the fall of pressure might have been due to absorption of oxygen by the mercury, another experiment was made in a similar way, but filling the bulb with dry nitrogen. The pressure fell as before and at about the same rate:

Time.	Fall of pressure in bulb containing radium.	$\Delta p.$	$\frac{\Delta p}{\Delta t}$
0 days	0.0 mm.	—	—
22 „	2.3 „	2.3 mm.	0.10
35 „	3.9 „	1.6 „	0.12

Thus very little of the effect could have been due to absorption of oxygen, and the increase in pressure obtained in the decomposition of ammonia does not represent the total decomposition. The preliminary fall of pressure in the ammonia experiment is thus partly accounted for, apart from the presence of air. The actual rate of decrease at the beginning of the ammonia experiment was about double that in the nitrogen experiment. As the fall of pressure due to this cause is so large, and, moreover, probably differs for different gases, it is impossible at present to calculate with any exactness the rate of decomposition of ammonia. It would appear, however, to be a reaction of the first order. As a rough approximation, the 5 milligrams of radium bromide decomposed 0.01 milligram of ammonia per day.

UNIVERSITY COLLEGE,
CARDIFF.

XVII.—*The Identity of Xanthaline and Papaveraldine.*

By BESSIE DOBSON and WILLIAM HENRY PERKIN, jun.

DURING the course of their valuable investigations on the constituents of opium, Messrs. T. and H. Smith (*Pharm. J.*, 1893, p. 793) described the isolation of a colourless alkaloid melting at 206° , which exhibited the characteristic property of forming yellow salts, and was therefore named xanthaline. This substance, which occurs in opium only in minute quantities, was isolated in a pure condition, and analyses of the alkaloid itself, as well as of its hydrochloride and reduction product (hydroxanthaline), seemed to indicate that its formula was $C_{37}H_{36}O_9N_2$. With a view to determine its nature, Messrs. T. and H. Smith sent the authors a quantity of this alkaloid, and a portion of it was recrystallised

from methyl ethyl ketone, in which it dissolved very sparingly in the cold, but much more readily on boiling. The hot solution, when allowed to cool slowly, deposits the alkaloid in colourless scales, which melt sharply at 207° or 210° (corr.):

0.1382 gave 0.3444 CO_2 and 0.0686 H_2O . $\text{C}=68.0$; $\text{H}=5.5$.

0.2398 „ 8.3 c.c. N_2 at 16° and 761 mm. $\text{N}=4.0$.

0.3443, heated with hydriodic acid by Perkin's modification of Zeisel's method, yielded 0.8884 AgI . $\text{MeO}=34.1$.

$\text{C}_{20}\text{H}_{19}\text{O}_5\text{N}$, containing 4 MeO , requires $\text{MeO}=35.1$ per cent.

These numbers agree closely with those obtained by Messrs. T. and H. Smith, who give four analyses of the alkaloid, the mean of which is $\text{C}=67.8$; $\text{H}=5.6$; $\text{N}=4.3$, and it will be seen that these percentages correspond with the formula $\text{C}_{20}\text{H}_{19}\text{O}_5\text{N}$, which requires $\text{C}=68.0$; $\text{H}=5.4$; $\text{N}=3.9$ per cent. In order to test the validity of this formula, the authors prepared the *platinichloride* of the alkaloid, which crystallised from dilute hydrochloric acid in orange-red prisms, and yielded, on analysis, the following result:

0.3500 gave 0.0611 Pt . $\text{Pt}=17.4$.

$(\text{C}_{20}\text{H}_{19}\text{O}_5\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ requires $\text{Pt}=17.4$ per cent.

The *methiodide* was next prepared by heating the alkaloid (10 grams) with methyl iodide (10 c.c.) and methyl alcohol (40 c.c.) in a sealed tube in the steam-bath, when the substance, which at first is sparingly soluble, passed completely into solution, and, on cooling, characteristic orange stars separated in quantity on the sides of the tube. The crystals were collected and left exposed to the air for several days, the substance then melted at 132° , and yielded, on analysis, numbers agreeing with the formula $\text{C}_{20}\text{H}_{19}\text{O}_5\text{N} \cdot \text{MeI} \cdot 3\text{H}_2\text{O}$:

0.3578, dried at 100° , lost 0.0334 $\text{H}_2\text{O}=9.3$.

0.7204 „ 105° „ 0.0756 $\text{H}_2\text{O}=10.5$.

0.1570 gave 0.0650 AgI . $\text{I}=22.4$.

$\text{C}_{20}\text{H}_{19}\text{O}_5\text{N} \cdot \text{MeI} \cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=9.8$; $\text{I}=23.1$ per cent.

This methiodide was then recrystallised several times from methyl alcohol, from which it separated in brilliant yellow prisms, which melted at 194° , and had the composition $\text{C}_{20}\text{H}_{19}\text{O}_5\text{N} \cdot \text{MeI} \cdot \text{H}_2\text{O}$:

0.1089 gave 0.1982 CO_2 and 0.0469 H_2O . $\text{C}=49.6$; $\text{H}=4.8$.

0.1565 „ 0.0710 AgI . $\text{I}=24.5$.

$\text{C}_{20}\text{H}_{19}\text{O}_5\text{N} \cdot \text{MeI} \cdot \text{H}_2\text{O}$ requires $\text{C}=49.1$; $\text{H}=4.7$; $\text{I}=24.7$ per cent.

Fusion with Potassium Hydroxide.—In this experiment, potassium hydroxide (30 grams) was mixed with water (5 c.c.), just fused in a nickel crucible, and then xanthaline (10 grams) added; the flame was at once removed, and the fusion stirred for two or three minutes, and until the alkaloid was completely decomposed. The crucible was then plunged into hot water, the oil which

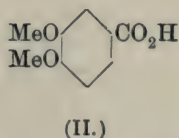
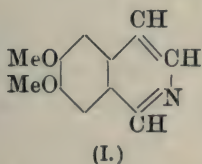
separated extracted with ether, the ethereal solution dried over solid potassium hydroxide and evaporated, when an oil remained which, on exposure to the air, soon solidified. After contact with porous porcelain, the substance was crystallised from ether or light petroleum, from both of which solvents it separated as a colourless, crystalline powder:

0.1112 gave 0.2846 CO_2 and 0.0579 H_2O . $\text{C}=69.7$; $\text{H}=5.8$.

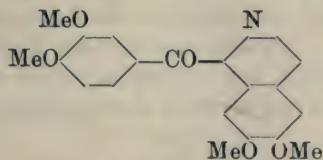
0.1860 „, 11.2 c.c. N_2 at 15° and 758 mm. $\text{N}=7.0$.

$\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$ requires $\text{C}=69.8$; $\text{H}=5.8$; $\text{N}=7.4$ per cent.

This substance, which melts at 94.5° and is obtained in a yield of at least 35 per cent., is dimethoxyisoquinoline (I). The alkaline solution, from which this substance had been extracted, yielded, on acidifying, a solid acid, which, after crystallisation from water, melted at 179.5 , and was easily recognised as veratric acid (II):



The consideration of all these facts seemed to show that the alkaloid xanthaline most probably has the constitution:



that is to say, that it was identical with papaveraldine, the substance which Goldschmiedt (*Monatsh.*, 1885, **6**, 956) first obtained by the oxidation of papaverine with permanganate. In order to test this supposition, a quantity of papaveraldine was prepared from papaverine, and the direct comparison proved conclusively that it was identical with xanthaline. Both melted at 208° , and, when intimately mixed, there was no alteration in the melting point. In describing the fusion of papaveraldine with potassium hydroxide, Goldschmiedt (*loc. cit.*) does not appear to have observed that dimethoxyisoquinoline is a crystalline substance, but we satisfied ourselves that, when papaveraldine from papaverine is fused with potassium hydroxide under the conditions described above, the dimethoxyisoquinoline obtained crystallises and melts at 94.5° .

It is, of course, impossible to say whether papaveraldine is

actually present in opium, or whether it is formed from papaverine during the complicated treatment which is necessary before it can be separated from the other constituents of opium.

THE UNIVERSITY,
MANCHESTER.

XVIII.—*Organic Derivatives of Silicon. Part XIV.* *The Preparation of Tertiary Silicols.*

By FREDERIC STANLEY KIPPING and JOHN EDWARD HACKFORD,
A.I.C., B.Sc.

VARIOUS tertiary silicols, $R_3Si \cdot OH$, have been obtained incidentally in the course of these investigations, and have been very briefly described in previous papers. In these cases the compounds were prepared by the hydrolysis of the tertiary chlorides, R_3SiCl , a method which suffers from the serious disadvantage that the tertiary chlorides are themselves obtained only with considerable difficulty, and, generally speaking, are not easily separated from accompanying by-products.

A procedure promising more satisfactory results was not far to seek. On the presumption that the behaviour of the silicones, R_2SiO , would be analogous to that of the ketones, it was only necessary to prepare the silicones by the hydrolysis of the dichlorides, R_2SiCl_2 (which are usually obtained much more easily than the trichlorides), and to treat these silicones with a Grignard reagent.

That a silicone would react with a magnesium alkyl or aryl halogen compound giving ultimately a tertiary silicol was, of course, a natural deduction to base on the known relationship of silicon to carbon. On the other hand, the very great dissimilarity between the silicones and the ketones in their general chemical behaviour, which was brought out by a study of benzylethylsilicone (Robison and Kipping, *Trans.*, 1908, **93**, 439), pointed to the possibility that this anticipation might not be realised.

As a matter of fact, the silicones were found to react with the Grignard reagents in a normal manner, and it is perhaps hardly too much to say that this is the first instance in which the silicones have been proved to show any analogy to the ketones in chemical behaviour.

Several tertiary silicols were prepared by the method here indicated; the yields were generally satisfactory, and the products, as a rule, did not contain any considerable proportion of the corre-

sponding oxides, $R_3Si \cdot O \cdot SiR_3$, into which the silicols are so prone to pass.

The silicones which were used in the earlier experiments were the crude liquid substances which were obtained by the decomposition of the purified dichlorides with water; these silicones, therefore, probably consisted to a considerable extent of the térmolecular polymerides, $(R_2SiO)_3$. As these preparations gave, nevertheless, good yields of the desired products, it seemed to follow that the termolecular silicones were resolved into the unimolecular compounds by the action of the Grignard reagents. This conclusion was borne out by the results of experiments with the pure termolecular form of dibenzylsilicone, which was found to yield the tertiary silicol, $SiMe(CH_2 \cdot C_6H_5)_2 \cdot OH$, after treatment with magnesium methyl iodide.

It was also found, as was of course to be expected in view of the results just mentioned, that a dihydric silicol, such as dibenzylsilicol, $Si(CH_2 \cdot C_6H_5)_2(OH)_2$, could be converted into a tertiary silicol by the method in question.

As the relatively very stable termolecular silicones are attacked by the Grignard reagents, and as these polymerides probably contain the grouping $R_2Si \cdot O \cdot SiR_2$, it seemed possible that the oxides $R_3Si \cdot O \cdot SiR_3$ might likewise react with the magnesium compounds, and yield, ultimately, a tertiary silicol and a silicane. Experiments, however, showed that the oxides remained unchanged even after they had been heated strongly with magnesium alkyl bromides.

The above method for the preparation of silicols is applicable, of course, in the case of asymmetric compounds, $R^1R^2R^3Si \cdot OH$, as well as in that of symmetrical silicols, $R^1R^2Si \cdot OH$ and $R_3Si \cdot OH$; the latter, however, it was found, may also be obtained, and perhaps more conveniently, by the interaction of an aryl (or alkyl) derivative of metasilicic acid and a Grignard reagent. Triphenylsilicol, for example, may be prepared by treating phenylmetasilicic acid, $C_6H_5 \cdot SiO \cdot OH$, with magnesium phenyl bromide, and tribenzylsilicol may be obtained from benzylmetasilicic acid in a corresponding manner. As is well known, in preparing tertiary alcohols from carboxylic acids, it is customary to employ the acids in the form of their esters; whether this is necessary or not in the case of the carboxylic acids, it is certainly not so as regards the silicic acids; the latter may be directly treated with the Grignard reagents.

In preparing phenylmetasilicic acid from the trichloride $SiPhCl_3$, it was found that hydrolysis with cold or even with hot water gave the acid as a viscous compound which was readily soluble in many organic solvents; hydrolysis with steam, on the other hand, resulted

in the formation of a vitreous solid, which was insoluble in all the common organic solvents and appeared to be the (polymerised) anhydride of the acid.

EXPERIMENTAL.

Benzyl-diethylsilicol, $C_6H_5 \cdot CH_2 \cdot SiEt_2 \cdot OH$.

Benzylethylsilicone, obtained by the decomposition of benzylethylsilicon dichloride with water (Trans., 1907, **91**, 720), was carefully dried at 100° , and the oil, which probably consisted partly of the termolecular compound (Robison and Kipping, *loc. cit.*), was then gradually added to an ethereal solution of magnesium ethyl bromide ($1\frac{1}{2}$ mols.). After the ether had been distilled off, the residue was heated at about 190° during one hour. When cold, the product was treated with water, and the oil which separated was extracted with ether and distilled under a pressure of 40 mm. The thermometer rose rapidly to 165° , at which temperature about 60 per cent. of the liquid passed over, and only a small quantity of a residue of high boiling point was obtained. Immediately after redistillation a sample of the liquid, boiling at $165^\circ/40$ mm., was analysed:

0.5572 gave 0.1698 SiO_2 . Si = 14.3.

$C_{11}H_{18}OSi$ requires Si = 14.6 per cent.

Benzyl-diethylsilicol is a colourless, mobile liquid, and is miscible with most of the common solvents. In the course of a day the clear, bright silicol became cloudy and deposited globules of water, an indication that it was undergoing a spontaneous transformation into the oxide. This change, however, occurred very slowly, and when redistilled the next day most of the liquid passed over below $167^\circ/40$ mm.

It was found by Martin and Kipping (Trans., 1909, **95**, 303) that tribenzylsilicol could be converted into tribenzylsilicyl chloride with the aid of acetyl chloride. If therefore other silicols could be transformed into the corresponding chlorides in a similar manner, these chlorides might then be employed for the preparation of various silicanes by the method previously used for this purpose. In order to test this possibility, benzyl-diethylsilicol was heated with a large excess of acetyl chloride during three hours, and the product was then distilled. Most of the liquid, excluding the acetyl chloride, passed over from 155° to $165^\circ/15$ mm., and a small proportion, consisting probably of the oxide, from 200° to 250° .

The fraction of lower boiling point contained only 5 per cent. of combined chlorine ($C_{11}H_{17}Cl$ contains 16.5 per cent. of chlorine), and was again heated with a large excess of acetyl chloride, but the product did not afford the desired chloride in anything approaching a condition of purity.

Benzylethylpropylsilicol, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{SiEtPr}\cdot\text{OH}$.

Benzylethylsilicone, prepared in the same way as the sample used in the preceding experiment, was added to an ethereal solution of magnesium propyl bromide ($1\frac{1}{2}$ mols.). The ether was distilled, and the residue heated at about 190° during one hour. The oily product which separated on the addition of water was extracted with ether and distilled under diminished pressure. Almost the whole of the liquid passed over between 169° and $174^\circ/40$ mm., and there was very little residue.

The freshly prepared silicol was analysed:

0.3264 gave 0.0964 SiO_2 . Si = 13.9.

$\text{C}_{12}\text{H}_{20}\text{OSi}$ requires Si = 13.6 per cent.

This compound has already been described (Kipping, Trans., 1907, **91**, 223), and the observation that the distilled product becomes turbid when kept at the ordinary temperature, with formation of benzylethylpropylsilicic oxide and water, was confirmed.

Phenylmethylethylsilicol, $\text{SiMeEtPh}\cdot\text{OH}$.

The phenylethylsilicone used in this and the following experiment was prepared by the hydrolysis of phenylethylsilicon dichloride (Marsden and Kipping, Trans., 1908, **93**, 208), and was treated with magnesium methyl iodide in the manner described in previous cases. When the product was distilled under diminished pressure, it yielded a large fraction, boiling constantly at $115^\circ/17$ mm.

This preparation was immediately analysed:

0.3780 gave 0.1406 SiO_2 . Si = 17.5.

$\text{C}_9\text{H}_{14}\text{OSi}$ requires Si = 17.0 per cent.

Phenylmethylethylsilicol is a colourless, mobile liquid, practically insoluble in water. In the course of half an hour, the clear, bright product became distinctly turbid, and drops of water gradually separated, but the transformation into the oxide seemed to be only very partial.

Phenyldiethylsilicol, $\text{SiEt}_2\text{Ph}\cdot\text{OH}$.

Phenylethylsilicone was treated with magnesium ethyl bromide under the conditions previously described in other cases, and the product was separated in the usual manner. When distilled under diminished pressure, most of the liquid passed over between 160° and $170^\circ/60$ mm., and from this fraction the pure silicol was isolated as a colourless, mobile liquid, boiling at $165^\circ/60$ mm.

An analysis of the freshly prepared substance was made:

0.3438 gave 0.1172 SiO_2 . $\text{Si} = 16.0$.

$\text{C}_{10}\text{H}_{16}\text{OSi}$ requires $\text{Si} = 15.7$ per cent.

Like most of the other silicols, this compound became turbid in the course of some hours, and changed spontaneously into the corresponding oxide and water. The product was redistilled after it had been kept for some time, and a fraction boiling at $208\text{--}210^\circ/40$ mm. was collected; this substance probably consisted of phenyldiethylsilicyl oxide, but silicon estimations gave unsatisfactory results, owing to the impossibility of burning away the whole of the carbon.

Dibenzylmethylsilicol, $\text{SiMe}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2\cdot\text{OH}$.

Termolecular dibenzylsilicone (m. p. 98°), obtained from dibenzylsilicon dichloride by the method already described (Robison and Kipping, *Trans.*, 1908, **93**, 440), was treated with an ethereal solution of magnesium methyl iodide, the ether was distilled, and the residue was heated at about 200° during an hour. The oily product, isolated in the usual manner, when distilled under diminished pressure boiled very constantly at $240\text{--}242^\circ/60$ mm., and only a small proportion passed over outside these limits. The freshly prepared liquid was analysed:

0.4470 gave 0.1130 SiO_2 . $\text{Si} = 11.9$.

$\text{C}_{15}\text{H}_{18}\text{OSi}$ requires $\text{Si} = 11.7$ per cent.

Dibenzylmethylsilicol is a colourless, mobile liquid, practically insoluble in water, but miscible with organic solvents.

Dibenzylmethylsilicyl Oxide, $[\text{SiMe}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2]_2\text{O}$.

The pure silicol just described gradually changed when it was left at the ordinary temperature, and after about a fortnight's time it yielded colourless crystals, which were separated and recrystallised from ether:

0.3414 gave 0.0912 SiO_2 . $\text{Si} = 12.5$.

0.3496 „ 0.9842 CO_2 and 0.2372 H_2O . $\text{C} = 76.6$; $\text{H} = 7.5$.

$\text{C}_{30}\text{H}_{34}\text{OSi}_2$ requires $\text{Si} = 12.2$; $\text{C} = 77.1$; $\text{H} = 7.3$ per cent.

These analyses and the manner of formation of this crystalline product show that it is *dibenzylmethylsilicyl oxide*, produced by the spontaneous decomposition of the silicol. It melts at 56° , and is readily soluble in ether, chloroform, or benzene, and moderately easily so in alcohol.

Conversion of Dibenzylsilicol into a Tertiary Silicol.

The action of magnesium methyl iodide on the β -form of dibenzylsilicol, $\text{Si}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2(\text{OH})_2$, described by Robison and Kipping

(Trans., 1908, **93**, 453), was also investigated. As the first result would probably be the conversion of the dihydric silicol into the silicone and water, a large excess of the Grignard reagent was used. A vigorous reaction occurred at first, and after a procedure described in previous cases a colourless oil was obtained. This product, like that obtained from dibenzylsilicone, boiled very constantly at $240\text{--}242^{\circ}/60\text{ mm.}$, from which fact it was concluded that the oil consisted of dibenzylmethylsilicol. In order to hasten the change into the oxide, the sample was heated at its boiling point under atmospheric pressure during about an hour, and was then allowed to cool. The next morning the sample was a pasty, crystalline mass, and after recrystallisation from ether, the solid product melted at 56° , which is the melting point of dibenzylmethylsilicly oxide.

Treatment of Silicyl Oxides with the Grignard Reagents.

As already stated, the oxides or ethers of the general formula $(R_3Si)_2O$ seem to be unchanged by the Grignard reagents. Experiments were made with benzylethylpropylsilicly oxide and with tribenzylsilicly oxide, which were finally heated at about 200° during an hour with magnesium propyl bromide and magnesium ethyl bromide respectively; in both cases, as far as could be ascertained, the original substance was recovered unchanged.

Tertiary Silicols from Substituted Metasilicic Acids.

Benzylmetasilicic acid, prepared by decomposing benzylsilicon trichloride with cold water, was treated with a large excess of an ethereal solution of magnesium benzyl chloride, and after the ether had been distilled, the residue was heated slowly up to about 220° . The product was then cooled, treated with water, and submitted to steam distillation until free from dibenzyl. The pasty mass which then remained was separated with the aid of ether and distilled under diminished pressure (20 mm.). The fraction collected from about 250° to 300° quickly solidified, and when crystallised from a mixture of chloroform and light petroleum yielded a pure sample of tribenzylsilicol. The yield was not good (only 5 grams of the pure silicol from 14 grams of the acid), and a large proportion of the crude product, probably unchanged acid, did not distil below $300^{\circ}/20\text{ mm.}$

Phenylmetasilicic acid, prepared from phenylsilicon trichloride, was treated with a large excess of magnesium phenyl bromide, and after the mixture had been heated to about 220° , the product of the reaction was separated from diphenyl and submitted to distillation. The fraction collected from about 270° to $300^{\circ}/14\text{ mm.}$,

solidified when cooled, and consisted almost entirely of triphenylsilicol; about 5 grams of the pure silicol were obtained from 10 grams of the acid.

Phenylmetasilicic Acid.

This compound was prepared long ago by Ladenburg by the hydrolysis of phenylsilicon trichloride with dilute ammonium hydroxide solution. The substance thus obtained is, when dried, a transparent, vitreous, brittle solid, and is readily soluble in ether and many other organic liquids, as well as in a solution of potassium hydroxide.

When phenylsilicon trichloride is hydrolysed with cold water, or even when it is poured into hot water, it gives a product having the above properties, but under certain conditions a very different result is obtained. This observation was made in the course of some experiments on the preparation of diphenylsilicon dichloride by the interaction of silicon tetrachloride, bromobenzene, and magnesium in presence of ether. Some fractions of low boiling point resulting from this preparation, and consisting of a mixture of bromobenzene and phenylsilicon trichloride, were directly treated with steam in order to remove the bromobenzene and obtain phenylmetasilicic acid. Instead of an oily residue of phenylmetasilicic acid, a white, brittle solid remained.

In order to ascertain the nature of this product, some pure phenylsilicon trichloride was prepared and directly treated with steam; it was rapidly transformed into a white solid, which was separated and repeatedly extracted with ether in order to free it from phenylmetasilicic acid, but very little (about 1 per cent.) of this substance was obtained. As the residue was insoluble in all the many organic liquids which were tried, it was dried at 120° and analysed; two different preparations gave the following results:

0.3308 gave 0.1536 SiO_2 . Si = 21.8.

0.3344 „ 0.1546 SiO_2 . Si = 21.7.

0.1700 „ 0.3460 CO_2 and 0.0596 H_2O . C = 55.5; H = 3.9.

$(\text{C}_6\text{H}_5\cdot\text{SiO})_2\text{O}$ requires Si = 21.9; C = 55.6; H = 3.9 per cent.

In making the combustion, the substance was previously mixed with copper oxide, as great difficulty was experienced in the silicon estimations in getting rid of the whole of the carbon.

The method of formation of this solid and the analytical results show that it is the anhydride of phenylmetasilicic acid. It is slowly acted on by a concentrated solution of aqueous alcoholic potash, and apparently is converted into a potassium salt of phenylmetasilicic acid; benzene is not formed in appreciable quantities, and after the alcohol is expelled, the solution gives with mineral acids after

some time a precipitate which resembles phenylmetasilicic acid in all its properties.

Although the anhydride is so readily formed from phenylsilicon trichloride, it is not readily produced when the acid is heated at 100°; a sample of the acid which had been heated during many hours still dissolved readily in ether.

The authors gratefully acknowledge the financial assistance for which they are indebted to the Government Grant Committee of the Royal Society.

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XIX.—*Intramolecular Rearrangements of Diphenylmethane o-Sulphoxide.*

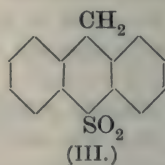
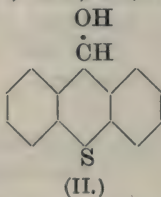
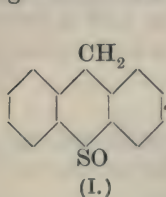
By THOMAS PERCY HILDITCH and SAMUEL SMILES.

THE changes which the ortho-sulphoxides of diphenylamine suffer on treatment with acid reagents (Trans., 1909, **95**, 1253; 1910, **97**, 186, 1112, 1559) demonstrate the instability of the thionyl group and the tendency of sulphur at that stage of oxidation to revert to the bivalent state through the intermediate phase of the sulphonium arrangement. Further illustration of this property of the thionyl group has been found in the simpler hydroxy-aromatic sulphoxides (Trans., 1910, **97**, 2248), which are converted into halogen derivatives of the sulphides on being heated with halogen acids. With these substances the intermediate sulphonium derivatives are more difficult to detect, chiefly on account of their inferior stability; but in experiments which are now being conducted some definite evidence of their existence has been obtained.

In extending this inquiry, we have first turned our attention to the behaviour of diphenylmethane *o*-sulphoxide (I), and, on account of the close structural resemblance between this substance and the corresponding derivative of diphenylamine, it was anticipated that a comparison of the behaviour of the two series would yield information on the mechanism of the reaction beyond that already obtained.

In order to obtain this sulphoxide, thioxanthen was oxidised with hydrogen dioxide in acetic anhydride solution, in accordance with the method which has been found suitable for the oxidation of thio- to thionyl compounds. The product melted at 109°, and gave analytical data corresponding with the required substance; but the

isomeric thioxanthenol (II) has recently been obtained by F. Mayer from the reduction of thioxanthone, and it is described by him as melting at 103—105° (*Ber.*, 1909, **42**, 1134).



It therefore appeared possible that the products of the two reactions, namely, the oxidation of thioxanthen and the reduction of thioxanthone, might be identical, and since no direct proof of the constitution of the substance obtained by reducing thioxanthone has ever been given, it became necessary more completely to demonstrate the constitution of the two substances.

*Constitution of Thioxanthenol and of Diphenylmethane
o-Sulphoxide.*

That the products from the two sources are evidently different is shown by the melting point of a mixture of approximately equal quantities; it is indefinite, and lies in the neighbourhood of 75—80°. The structure of thioxanthenol formed by reduction of thioxanthone is shown by the following facts:

(i) It is converted into thioxanthone by oxidation with the calculated amount of potassium permanganate in cold glacial acetic acid.

(ii) It yields a benzoyl derivative when treated with benzoyl chloride in pyridine solution.

(iii) It reacts with phenylcarbimide; the product, however, appears to be unstable, decomposing into diphenyl carbamide.

Further, it is clear that the product melting at 109°, which is formed by oxidising thioxanthen with hydrogen dioxide under the conditions described in the experimental part of this paper, is the required diphenylmethane *o*-sulphoxide (II), for

(i) It yields diphenylmethane *o*-sulphone (III) when treated with the calculated amount of potassium permanganate in cold glacial acetic acid.

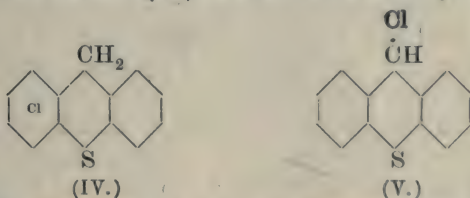
(ii) It does not react with phenylcarbimide, nor does it yield a benzoyl or acetyl derivative with the usual reagents.

The Action of Acids on Thioxanthenol.

The action of acid reagents on thioxanthenol has been mentioned by Werner (*Ber.*, 1901, **34**, 3311) at the conclusion of his study

of the carboxonium salts. Werner found that solutions of thioxanthenol became coloured by the addition of mineral acids, and when bromine vapour was passed into the solution of thioxanthenol in aqueous hydrogen bromide, he obtained a crystalline perbromide; but since no analytical data was given, we have repeated and extended these experiments. The carbothionium chloride (VI) is obtained as a brick-red, crystalline precipitate when an ethereal solution of thioxanthenol is saturated with hydrogen chloride. This substance is not sufficiently stable to be obtained in a condition suitable for analysis, but it yields a stable, red, double salt with ferric chloride. Werner (*loc. cit.*) has pointed out that xanthenol may be regarded as the pseudo-base of the carboxonium salts, and that the same relation probably holds between thioxanthenol and the carbothionium salts, and we find, in accordance with this view, that the red salt is reconverted into thioxanthenol by the action of alkaline reagents.

At the same time, we have succeeded in obtaining an intermediate substance in this change; when the carbothionium chloride is dried in a vacuum desiccator to remove excess of hydrogen chloride, it is converted into an isomeric colourless substance for which there are two alternative structures available, namely, those of the chlorothioxanthen (IV) and the thioxanthenyl chloride (V):



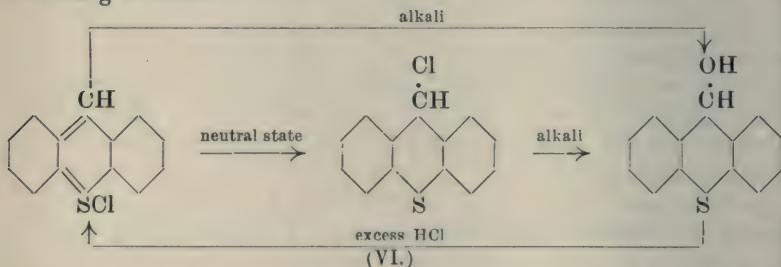
The former substance might be expected to be formed in accordance with the reaction which takes place between phenazothionium chloride and excess of hydrogen chloride (Trans., 1910, 97, 1112) when chlorothiodiphenylamine is formed; but this structure for the substance now in question cannot be accepted, for the halogen is very easily removed by alkaline reagents or even by water, thioxanthenol being formed. The compound must therefore be regarded as the carbonium chloride.

The change effected on thus passing from the sulphonium to the carbonium chloride involves the removal of halogen from quadri-valent sulphur to carbon; and in the light of other work and the migration of halogen in aromatic compounds, especially that of Orton on the transformation of *N*-chloroacylarylamines (*Proc. Roy. Soc.*, 1902, 71, 156), it appears probable that the reaction takes place by the addition and subsequent removal of hydrogen chloride.

Moreover, this view of the process is confirmed by the recent

experiments of Gomberg and Cone (*Annalen*, 1910, **376**, 183), who find that the salts* obtained by the action of halogen acids on phenylthioxanthanol contain an additional molecule of halogen acid which is lost in the transformation to the carbonium halide.

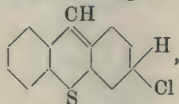
The conditions under which the reverse change of thioxanthanyl chloride into thioxanthonium salt takes place have not been clearly ascertained, but, so far as our experiments have been carried, it seems the mere presence of excess of acid is sufficient. The relations which hold between this group of substances are indicated by the following formulæ:



Conversion of Diphenylmethane o-Sulphoxide into Thioxanthonium.

Like thioxanthanol, the ortho-sulphoxide of diphenylmethane is converted by mineral acids into the thioxanthonium salts, but the speed with which this transformation takes place is less than in the former instance. This sulphoxide, however, cannot be regarded as the pseudo-base of thioxanthonium, for, as previously mentioned, thioxanthanol is formed by the action of alkaline reagents on the latter substance. At the same time, it is clear that by the successive application of the acid and alkaline reagents the diphenylmethane o-sulphoxide may be converted into thioxanthanol, the net result

* It is necessary to mention that Gomberg and Cone (*Annalen*, 1909, **370**, 142; 1910, **376**, 183) on account of certain analogies to triphenylcarbinol have recently advocated a quinocarbonium structure, for example,



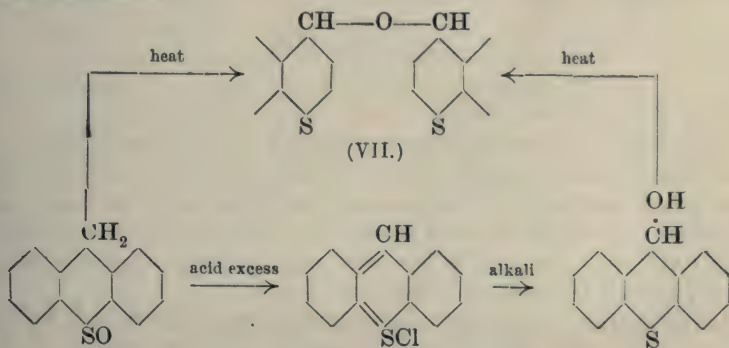
for these coloured salts as well as for those of the corresponding acridonium, azonium, xanthonium and azothionium series. We prefer, however, to retain the azonium, thionium, and oxonium structures which have been advocated for these substances by Hewitt (*Zeitsch. physikal. Chem.*, 1900, **34**, 9), Kehrman (*Annalen*, 1902, **322**, 1), Werner (*Ber.*, 1901, **34**, 3300) and others. Both Kehrman (*Annalen*, 1910, **372**, 287) and Hewitt and Thole (*Proc.*, 1910, **26**, 225) have recently opposed the view of Gomberg and Cone, and, so far as the thio-compounds are concerned, the present authors have yet other reasons for disagreement with the quinocarbonium structure, but the publication of this is deferred until the experiments from these other sources have been completed.

of the change being the transference of oxygen from sulphur to carbon. It is interesting to find that this transference may be effected by the aid of heat alone.

Thioxanthenol behaves under the influence of heat like its congener, xanthenol (R. Meyer, *Ber.*, 1896, **29**, 1276), for, when heated alone or in glacial acetic acid to about 120°, it furnishes the thioxanthenyl oxide (VII); and the same substance is formed when diphenylmethane *o*-sulphoxide is treated in a similar manner, the sole difference being that the yields are somewhat smaller, and more prolonged heating is required. Further evidence of this change may be adduced from the behaviour of thioxanthen with hydrogen dioxide in glacial acetic acid solution. If the boiling solution of this substance is mixed with excess of hydrogen dioxide good yields of diphenylmethane *o*-sulphone are obtained. On the other hand, if a cold solution of thioxanthen in acetic acid containing about one molecular proportion of the oxidising agent is heated gradually to the boiling point, the chief product is thioxanthone. Evidently the latter circumstance is due to the conversion of the sulphoxide, which is slowly formed by the dilute peroxide into thioxanthenol, the latter in turn being oxidised to thioxanthone. Under the first set of conditions, the large excess of peroxide completes the oxidation of the thionyl group before the change to thioxanthenol has proceeded to any appreciable extent.

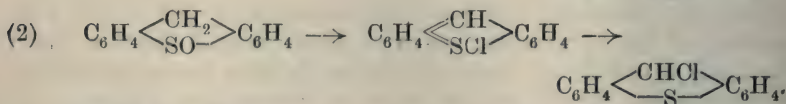
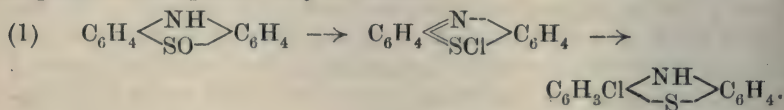
Moreover, it may be remarked that the mixture of sulphoxide and thioxanthenol, which melts indefinitely at 75–80°, if heated for a short time to about 110° and then allowed to cool and solidify, melts on re-heating at a much higher temperature in the neighbourhood of 100–102°. So far as we are aware, diphenylmethane *o*-sulphoxide is the only substance of that class which melts at a lower temperature than the corresponding sulphide, and it is possible that the anomaly is due to this isomerising action of heat.

The following formulæ summarise the relations which connect these substances:

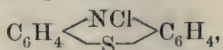


The probable mechanism of the conversion of the sulfoxide to the thioxanthonium salt is discussed in a subsequent paragraph.

Regarding the relations between these derivatives of thiodiphenylmethane from a general point of view, it is evident that they are closely parallel to those which have been previously observed (Trans., 1909, **95**, 1253; 1910, **97**, 186, 1112, 1559) with the thiodiphenylamine group, for in each series the quadrivalent sulphur of the thionyl group is reduced by the prolonged action of halogen acid to the bivalent state through the intermediate stage of an unsaturated sulphonium arrangement. Moreover, the same terminal stage has been observed with the simpler aromatic hydroxysulphoxides, and it is hoped that here, too, the intermediate sulphonium compound may be isolated:



There is, however, an interesting difference between the final products obtained in the two series, for in the thiodiphenylamine group the halogen finally enters the aromatic nucleus, whereas in the thiodiphenylmethane series it does not, but instead remains attached to the methane carbon atom. Armstrong (Trans., 1900, **77**; 1051), Orton (Trans., 1909, **95**, 14), and others have shown how easily the *N*-chloro-derivatives of acylarylamines are transformed into the aromatic halides by the intervention of free hydrogen chloride; and in view of the isolation of this carbonium chloride in the diphenylmethane series, it appears not improbable that the corresponding *N*-chloro-compound:

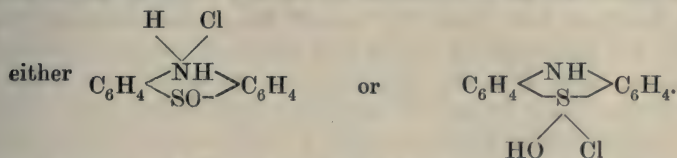


has a transitory existence during the action of hydrogen chloride on the phenazothionium salt.

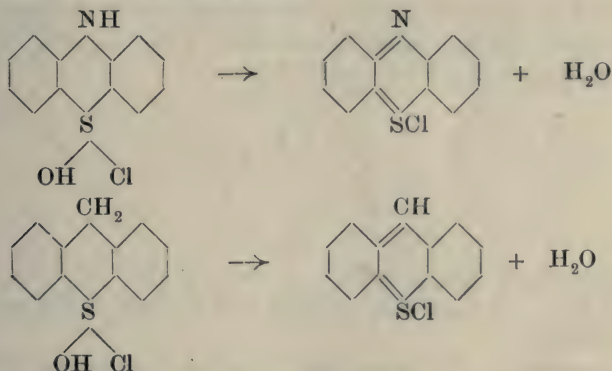
Turning to consider the mechanism by which these sulfoxides are converted into the corresponding azo- or carbo-thionium salts, the permissible assumption is made that in the two series the processes are alike in their essential features, although perhaps minor differences may arise from the more pronounced basic power of the thiodiphenylamine compounds.

Investigation of the latter group has shown (Barnett and Smiles, Trans., 1910, **97**, 186) that the reaction does not consist of the

mere transference of hydrogen from the amino- to the thionyl group, but that it depends on the preliminary formation of a salt. The subsequent observation (Brady and Smiles, Trans., 1910, **97**, 1559) that the monohydrochloride of trichlorothiodiphenylamine sulphoxide is very easily converted—merely by warming in certain solvents—into the azothionium compound indicates that it is only the mono-acid salt which is essential, but it was difficult to decide with certainty whether this is the amine or thionyl hydrochloride:



When, however, it is considered that the *o*-sulphoxide of diphenylmethane contains only one group of basic function, it becomes clear that not only is the formation of a mono-acid salt sufficient, but that this essential must be the sulphoxide salt. Finally, on regarding the structures of these substances:



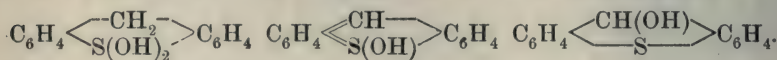
it is seen that the simplest way in which the formation of the thionium salts can take place is by the elimination of water, and we consider that this conception of the process affords a satisfactory explanation of every case of this transformation which has hitherto been studied.

Without entering into the details of each case in particular, it may be sufficient to discuss one example which is of an exceptional nature. Of all the nitro-derivatives of diphenylamine *o*-sulphoxide, the tetranitro-compound is the most difficult to convert into the azothionium form by the action of mineral acids, but it is the only one of them which is transformed by the action of heat. This substance is also exceptional in containing an additional molecular proportion of water, which is only removed with great difficulty,

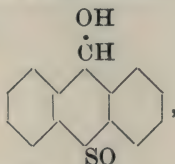
and thus weight is given to the suspicion that the thionyl group may here exist in the ortho-condition, $>\text{S}(\text{OH})_2$.

The exceptional behaviour of this substance is thus readily explained, for a thionyl compound which is capable of separate existence in this form would, according to the hypothesis now advanced, be more readily converted by heat into the azothionium compound than one which is incapable.

Evidence for the existence of the thionyl group in this ortho-form has elsewhere been given by one of the present authors (*Trans.*, 1906, **89**, 697) and by others (for example, Fromm and Raiziss, *Annalen*, 1910, **374**, 90), and there can be no doubt that the salts which that group forms with acids are derived from that structure. On regarding the diphenylmethane *o*-sulphoxide from this point of view, it is seen that the somewhat complex transformation into thioxanthonium and thence into thioxanthanol is merely the successive removal of two hydroxyl groups from the thionyl group:

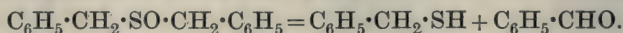


In order to ascertain whether this process can be continued until the methane carbon atom is saturated with oxygen, we have examined diphenylcarbinol *o*-sulphoxide:

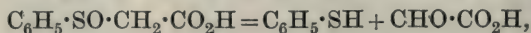


hoping to obtain thioxanthone from it by similar reactions. However, we have not been able to effect this rearrangement under the usual conditions.

In conclusion, it may be remarked that this transference of oxygen from thionyl to methylene in the thiodiphenylmethane series is not an isolated occurrence of that reaction, for a similar behaviour has been observed with open-chain compounds in which these groups are adjacent. Smythe (*Trans.*, 1909, **93**, 349), for example, has noticed the formation of benzaldehyde and benzyl mercaptan from benzyl sulphoxide and dry hydrogen chloride:

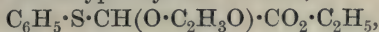


Also, Pummerer (*Ber.*, 1909, **42**, 2202) has met with a similar behaviour in phenylsulphoxyacetic acid, which yields phenyl mercaptan and glyoxylic acid under the influence of mineral acids:



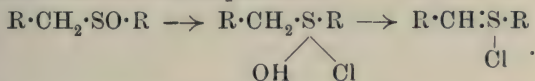
but he found that with the ester of this acid (*Ber.*, 1910, **43**, 1401)

the rearrangement may be carried out without rupture of the molecule, ethyl α -acetoxyphenylthiolacetate,



being obtained by the action of acetic anhydride.

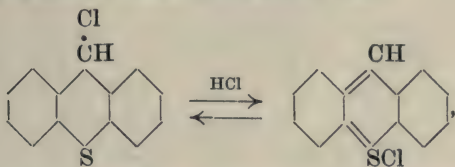
Pummerer has advocated the hypothesis (*Ber.*, 409, **42**, 2282; see also Fromm and Erfurt, *ibid.*, 3812) that these sulfoxides, containing the group $\cdot\text{CH}_2\cdot\text{SO}\cdot$, may owe their instability in presence of acids to a tendency to form an unsaturated sulphonium base which undergoes the observed decomposition:



Although no experimental evidence was advanced directly to support this conclusion, there can be little doubt in the light of the present experiments that it is correct. Pummerer, however, and apparently also Fromm (Fromm and Raiziss, *Annalen*, 1910, **374**, 90), seem to regard the sulphonium hydroxide and the methylene-sulfoxide as tautomeric. To justify this conclusion, it is necessary to isolate these unsaturated fatty sulphonium bases, and, if ever this be successful, we consider it very doubtful whether the hypothesis of tautomerism will be borne out, for the experiment with the ester of phenylsulphoxyacetic acid seems to point to the conversion of the sulphonium hydroxide into the hydroxy-acid.

At any rate, in the thiodiphenylmethane series there can be no question of tautomerism between the diphenylmethane *o*-sulphoxide and the carbothionium hydroxide, for the latter, when liberated from its salts with alkali, gives thioxanthenol and, so far as we are aware, not even a small quantity of the sulfoxide.

It appears, however, that in certain solvents an equilibrium between the thioxanthenyl chloride and carbothionium salt may be established by means of free hydrochloric acid:



for if excess of acid be added, the latter salt is formed, whilst if the acid be removed (see also Gomberg and Cone, *Annalen*, 1910, **376**, 183) the carbonium chloride is obtained.

EXPERIMENTAL.

The chief difficulty in the way of these experiments was the preparation of thioxanthen in sufficiently large quantities; but this

has been met by the convenient synthesis of that substance from *o*-thiolbenzoic acid and benzene in presence of sulphuric acid (Davis and Smiles, *Trans.*, 1910, **97**, 1290). Thioxanthone was then reduced to thioxanthen by Graebe and Schulthess's method (*Annalen*, 1891, **263**, 1), which consists in heating with phosphorus and hydriodic acid in sealed tubes. A specimen of the thioxanthen, which was employed in the following experiments, melted, after being recrystallised from light petroleum, at 128—129°, and gave the requisite analytical data. (Found, C=79.1; H=5.2. Calc., C=78.78; H=5.0 per cent.)

Oxidation of Thioxanthen.

(a) *With Hydrogen Dioxide in Acetic Anhydride: Diphenylmethane o-Sulphoxide*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{SO}_2\end{smallmatrix}\rangle\text{C}_6\text{H}_4$.—A solution of thioxanthen in acetic anhydride was gradually mixed with about twice the quantity of aqueous hydrogen dioxide necessary for complete conversion into sulphoxide. The mixture was then set aside at the atmospheric temperature, being shaken at frequent intervals. After the lapse of a short time the temperature increased, but this was not allowed to rise above 35°, the reaction being checked by immersing the vessel in melting ice. If the mixture was kept at about 30°, the reaction proceeded quietly, and was soon complete. When no further rise of temperature was observed after removing the vessel from the cooling-bath, the mixture was poured on powdered ice. When the pale yellow, crystalline precipitate had completely separated, it was collected and recrystallised from light petroleum, in which it is sparingly soluble, and *diphenylmethane o-sulphoxide* was obtained in soft flakes, melting at 109—110°:

0.1325 gave 0.3561 CO_2 and 0.0489 H_2O . C=73.28; H=4.10.

0.1214 „ 0.3240 CO_2 „ 0.0462 H_2O . C=72.78; H=4.2.

$\text{C}_{13}\text{H}_{10}\text{OS}$ requires C=72.90; H=4.6 per cent.

The compound is insoluble in water, and sparingly so in ether. When dry ferric chloride is added to a solution in the latter medium, a double salt is precipitated in fine, yellow needles. This behaviour has been observed with other aromatic sulphoxides (Hofmann and Ott, *Ber.*, 1907, **40**, 4930), and appears to be characteristic. The action of heat and acids on this sulphoxide is described later.

In the preparation of this substance, it is important to prevent the temperature rising above the limit mentioned, otherwise the reaction is apt to get out of control, and when this occurs the product is almost entirely diphenylmethane *o*-sulphone (m. p.

168—169°). Also, it is advisable to employ only small quantities—about 5 grams—of thioxanthen.

(b) *With Potassium Permanganate in Acetone.*—The sulphoxide may also be prepared by a process similar to that applied to *N*-methylthiodiphenylamine (Barnett and Smiles, *Trans.*, 1910, **97**, 188). The calculated amount of permanganate was added in small portions to a solution of thioxanthen in acetone, which was kept faintly acid with sulphuric acid during the reaction. After pouring the mixture into water, and removing any oxides of manganese by the addition of sulphurous acid, a quantity of the sulphoxide was obtained; but the yields were not good, the product being contaminated with sulphone.

(c) *With Hydrogen Dioxide in Acetic Acid: Diphenylmethane o-Sulphone.* $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{SO}_2 \end{smallmatrix} \text{C}_6\text{H}_4$, and Thioxanthone.—Excess of concentrated hydrogen dioxide was added to a boiling solution of thioxanthen in glacial acetic acid. The action proceeded vigorously, and the temperature was maintained at the boiling point for a few minutes.

On cooling the liquid, a quantity of diphenylmethane *o*-sulphone separated in colourless needles (m. p. 170°). (Found, C=67·8; H=4·2. Calc., C=67·8; H=4·3 per cent.) No other product was isolated from the reaction carried out under these conditions.

Other experiments were made in which approximately equimolecular proportions of hydrogen dioxide and thioxanthen were employed. In these experiments the peroxide was added to a cold dilute solution of thioxanthen in glacial acetic acid, the mixture being then slowly warmed to the boiling point. On cooling the contents of the flask, thioxanthone separated in the characteristic yellow needles. It melted at 209°, and was identified by a mixed melting-point determination.

The different course taken by the process of oxidation under these sets of conditions has been dealt with in the theoretical part of this paper.

Constitution of Diphenylmethane o-Sulphoxide.

(a) *Oxidation.*—Two grams of the sulphoxide were dissolved in cold glacial acetic acid, and an amount of potassium permanganate corresponding with one gram-atom of available oxygen for every gram-molecule of sulphoxide was gradually added. The reaction was assisted by shaking, and when it was complete the mixture was poured into cold water and then mixed with sulphurous acid. The colourless solid was collected, and finally crystallised from acetone.

Diphenylmethane sulphone was thus obtained in small, colourless

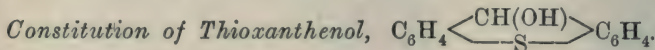
prisms, which melted at 169° (Graebe, *loc. cit.*, gives 168° , and Lapworth, *Trans.*, 1898, **73**, 408, gives $169-170^{\circ}$). (Found, C=67.61; H=4.37. Calc., C=67.82; H=4.35 per cent.)

(b) *Behaviour with Phenylcarbimide*.—A solution of the sulphoxide in excess of phenylcarbimide was set aside at the atmospheric temperature for some days; after the lapse of that time a very few crystals of diphenylcarbamide had separated, otherwise no interaction could be detected (compare thioxanthenol, p. 157).

(c) *Behaviour with Benzoyl Chloride*.—A slight excess of benzoyl chloride was slowly added to a cooled solution of the sulphoxide in pyridine. After being kept at the atmospheric temperature for twenty-four hours, the mixture was poured into excess of dilute aqueous sulphuric acid. The oil which then separated quickly solidified. The product was recrystallised from light petroleum, from which it separated in the soft crystals characteristic of the sulphoxide.

These melted at $109-110^{\circ}$, whether alone or mixed with a sample of diphenylmethane *o*-sulphoxide. No other product could be isolated from this reaction. It is evident that, under the conditions given above, diphenylmethane *o*-sulphoxide does not react with benzoyl chloride (compare thioxanthenol, p. 157).

It may be remarked that a mixture of this sulphoxide with thioxanthenol melts at a lower temperature than either—at about $70-75^{\circ}$ if nearly equal quantities be mixed.



We at first attempted the preparation of this substance by the method described by Werner (*Ber.*, 1901, **34**, 3310), who added zinc dust to thioxanthone, which was suspended in a boiling alcoholic solution of sodium ethoxide. The product obtained by this method, however, melted indefinitely at $150-155^{\circ}$, and appeared to be a mixture of at least two substances, and we therefore adopted the use of potassium ethoxide in place of sodium ethoxide, as recommended by F. Mayer (*Ber.*, 1909, **42**, 1132). The substance used in the following experiments melted, after being recrystallised from light petroleum, at $103-104^{\circ}$. (Found, C=72.8; H=4.66. Calc., C=72.9; H=4.67 per cent.)

The yield of the substance obtained by this method is not always good, and it varies considerably. So far as we have been able to ascertain, the yield is favoured by allowing the reduction to proceed vigorously, by excluding air from the vessel to prevent oxidation of the thioxanthenol, and by not allowing the temperature to rise too high on prolonging the reaction, otherwise thioxanthenyl oxide may be formed.

(a) Oxidation of thioxanthenol with potassium permanganate in glacial acetic acid was carried out in a manner precisely similar to that described with diphenylmethane *o*-sulphoxide.

The product crystallised from acetic acid in yellow needles, which melted at 209°, and possessed all the properties of thioxanthone. (Found, C=73·9; H=4·0. Calc., C=73·6; H=3·8 per cent.) The yield was good, and no other product was isolated.

(b) *Behaviour with Phenylcarbimide*.—A solution of dry thioxanthenol in phenylcarbimide, when kept at the atmospheric temperature, quickly gave a copious deposit of a crystalline substance. After the lapse of a few days this was collected. It was apparently a mixture, but after being twice or thrice recrystallised from absolute alcohol, it furnished diphenylcarbamide (m. p. 236—238°).

It is difficult to say whether this is formed by a decomposition of a carbamate during crystallisation, or by the mere withdrawal of water from the thioxanthenol. In any case, the behaviour of thioxanthenol with phenylcarbimide is quite different from that of diphenylmethane *o*-sulphoxide.

(c) Benzoylation of thioxanthenol was effected in pyridine solution with benzoyl chloride. The treatment of the reaction mixture was the same as that applied in the case of diphenylmethane *o*-sulphoxide (p. 156). The product, benzoylthioxanthenol, was crystallised from alcohol, when it was obtained in leaflets of a pale yellow tint; these melted somewhat indefinitely at 124—128°:

0·1040 gave 0·2859 CO₂ and 0·0414 H₂O. C=74·98; H=4·42.

C₂₀H₁₄O₂S requires C=75·48; H=4·4 per cent.

The interaction of acetyl chloride and thioxanthenol in pyridine solution furnished thioxanthenyl oxide (see p. 159), and the same substance was obtained by interaction with hot acetic anhydride. Thioxanthenol is further clearly distinguished from the diphenylmethane *o*-sulphoxide by the interaction with ferric chloride. When this substance is added to an ethereal solution of thioxanthenol, the red ferrichloride of thioxanthonium is obtained as a crystalline precipitate. The sulphoxide yields the normal yellow addition product.

Salts of Thioxanthonium, C₆H₄ << $\begin{smallmatrix} \text{CH} \\ \text{S} \end{smallmatrix}$ >> C₆H₄.

(a) *From Thioxanthenol*.—Thioxanthenol dissolves in concentrated sulphuric acid or in alcoholic hydrogen chloride, giving deep red solutions of the corresponding salts of thioxanthonium. The sulphate may be obtained in the solid state by adding a drop of sulphuric acid to an ethereal solution of thioxanthenol.

Thioxanthonium chloride was prepared by saturating an ethereal solution of thioxanthenol with dry hydrogen chloride at 0°. The

liquid rapidly assumed a deep red colour, and, when completely saturated with the acid, it deposited a copious crystalline precipitate. Thioxanthonium chloride crystallises in brick-red needles with a metallic lustre. It is readily soluble in alcoholic hydrogen chloride, and sparingly so in ether which has been saturated with that acid. It is rapidly hydrolysed by water or solvents such as alcohol, giving thioxanthenol. Analysis of this chloride was not directly effected, for after the crystalline material had been collected and immediately placed over alkali in a vacuum desiccator on porous earthenware, it was rapidly transformed into the colourless thioxanthenyl chloride.

For analysis the substance was converted into the stable ferrichloride. This substance was obtained by adding an ethereal solution of anhydrous ferric chloride to the deep red solution obtained by saturating thioxanthenol in ether with hydrogen chloride.

When prepared in this manner, *thioxanthonium ferrichloride* forms bright red needles, which melt at 193—194°:

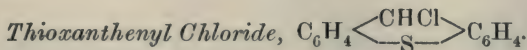
0.1313 gave 0.1889 CO₂ and 0.0287 H₂O. C=39.23; H=2.43.

0.1747 „ 0.0355 Fe₂O₃. Fe=14.22.

C₁₃H₉ClS, FeCl₃ requires C=39.5; H=2.28; Fe=14.18 per cent.

(b) *From Diphenylmethane o-Sulphoxide*.—The solution of this sulphoxide in concentrated sulphuric acid has the same appearance as that of thioxanthenol, and on adding water to it the latter substance is precipitated.

The action of alcoholic hydrogen chloride on the sulphoxide is slower than with thioxanthenol, but the red solution of thioxanthonium chloride is finally produced. The best method of preparing the chloride in the solid condition from the sulphoxide is to work in ethereal solution as with thioxanthenol. The product was identified by conversion to the ferrichloride mentioned in the foregoing paragraph. The crystalline sample obtained melted at 190°. (Found, C=39.66; H=2.8; Fe=14.20. Calc., C=39.50; H=2.28; Fe=14.18 per cent.)



When the solid thioxanthonium chloride is kept in a vacuum desiccator over solid alkali hydroxide to remove excess of acid, the red crystals of the substance rapidly break up and lose their colour, the mass finally becoming almost colourless. Analysis was conducted with a sample which had been dried in this manner:

0.1203 gave 0.2973 CO₂ and 0.0421 H₂O. C=67.47; H=3.89.

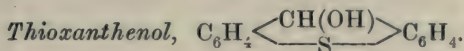
C₁₃H₉ClS requires C=67.11; H=3.87 per cent.

Reasons for assuming the carbonium structure for this substance have been given in a foregoing paragraph.

Thioxanthenyl chloride is soluble in ether, and melts at 112—113°; there is no doubt that in the pure condition the substance is colourless, the pale colour of these samples obtained being due to traces of enclosed thioxanthonium salt. The substance was not recrystallised on account of the extreme ease with which it is hydrolysed. Evidence of this hydrolysis is furnished by estimations of chlorine at intervals after preparation, the sample remaining over calcium chloride in a desiccator which was frequently opened:

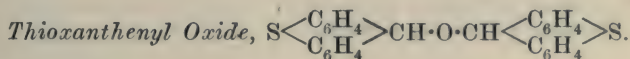
After one day, Cl=13·68; after three days, Cl=12·33; after five days, Cl=10·51.

$C_{13}H_9ClS$ requires Cl=15·27 per cent.



(a) *From Thioxanthenyl Chloride.*—Two experiments were performed; in one the chloride was saturated with water, and in the other with dilute alkali hydroxide. The solid material was extracted with ether, and finally crystallised from light petroleum. In each case thioxanthenol and thioxanthone were obtained; these were identified by their melting points, alone and mixed with other samples of these substances. There is no doubt that the latter substance is formed by oxidation of thioxanthenol by atmospheric oxygen.

(b) *From Thioxanthonium Salts.*—The various salts of thioxanthonium, for example, sulphate and chloride, are readily converted into thioxanthenol by excess of water. An experiment was also made with the ferrichloride, of which the details are given. The salt was triturated with cold aqueous alkali hydroxide, and the precipitate which then formed was collected, dried, and extracted with alcohol. The solution deposited thioxanthenol, melting at 103—105°. (Found, C=72·6; H=5·0. Calc., C=72·9; H=4·6 per cent.)



(a) *From Thioxanthenol.*—A few grams of this substance were heated in a bath at 120°. After the lapse of about one hour, the material had resolidified to a dark-coloured, crystalline cake. This was recrystallised from boiling glacial acetic acid, when thioxanthenyl oxide was obtained in pale yellow needles, which melted at 314—315°:

0.1401 gave 0.3918 CO_2 and 0.0558 H_2O . $\text{C}=76.25$; $\text{H}=4.43$.

$\text{C}_{26}\text{H}_{18}\text{OS}_2$ requires $\text{C}=76.08$; $\text{H}=4.39$ per cent.

The substance is very sparingly soluble in cold glacial acetic acid, and is decomposed by mineral acids, giving red solutions of thioxanthonium salts.

From the mother liquors of this preparation thioxanthone was isolated (m. p. 208° ; $\text{C}=73.4$; $\text{H}=4.5$. Calc., $\text{C}=73.5$; $\text{H}=3.7$ per cent.), being formed by oxidation of the thioxanthenol by atmospheric oxygen.

It was later found that thioxanthenyl oxide is formed in better yield and in a purer condition by boiling a solution of thioxanthenol in glacial acetic acid. The substance is rapidly deposited from the boiling solution in the crystalline state.

(b) *From Diphenylmethane o-Sulphoxide*.—The method employed was the same as that described with thioxanthenol, except that the heating was continued for a longer period. The yields of thioxanthenyl oxide was not so good as in the former case, and the substance was not so easily obtained in the pure condition. The sample obtained by recrystallisation of the product melted at 310° . (Found, $\text{C}=76.38$; $\text{H}=4.48$. Calc., $\text{C}=76.08$; $\text{H}=4.39$ per cent.)

As with thioxanthenol, much better yields are obtained by boiling the sulphoxide in glacial acetic acid; the oxide is then precipitated from the cooled liquid in an almost pure condition (m. p. $314\text{--}315^\circ$; $\text{C}=76.05$; $\text{H}=4.8$. Calc., $\text{C}=76.08$; $\text{H}=4.39$ per cent.).

When experiments were made with other boiling solvents, it appeared that the transformation of the sulphoxide depends not only on the temperature of ebullition, but on the nature of the liquid. For example, a solution of the sulphoxide in pyridine was boiled (115°) for some hours, but almost the whole of the sulphoxide employed was recovered (m. p. 109° ; $\text{C}=73.1$; $\text{H}=4.9$. Calc., $\text{C}=72.9$; $\text{H}=4.6$ per cent.).

In conclusion, we desire to express our thanks to the Research Fund Committee of the Society for a grant which has partly defrayed the cost of these experiments.

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XX.—o-Carboxyanilides of the Sugars.

By JAMES COLQUHOUN IRVINE and ALEXANDER HYND, M.A., B.Sc.
(Carnegie Scholar).

IN papers recently published from this laboratory it has been shown (Trans., 1908, **93**, 1429; 1909, **95**, 1545) that the condensation of reducing sugars with amino-compounds may take place in two distinct ways, according as the sugar reacts as an aldehyde or as a γ -oxide. One of the compounds discussed in this connexion was glucose-o-carboxyanilide, the reactions of which indicate that the linking of the sugar residue with anthranilic acid takes place through nitrogen. As this result bears directly on the general question of the formation of sugar complexes containing nitrogen, we have examined the behaviour of other sugars towards anthranilic acid, and have succeeded in preparing compounds analogous to glucose-o-carboxyanilide from galactose, rhamnose, mannose, and maltose. Condensation also proceeded in the case of fructose, but no definite compound was isolated, whilst lactose did not react. This negative result is in itself significant, as lactose is probably the only reducing sugar which forms a true aldehyde-ammonia compound.

The condensation proceeded easily in dilute alcoholic solution in the cold; all the compounds were found to react as acids, and the coupling of the anthranilic acid therefore takes place through the amino-group. In other respects, also, the carboxyanilides resemble the corresponding anilides closely, but are more unstable, so that it is impossible to confirm their structure by the methylation process (*loc. cit.*). In the following table it is shown that in each case the compounds display mutarotation which is strictly comparable with that undergone by the corresponding unsubstituted anilides and by the methylated anilides, for which the γ -oxidic structure has already been established.

Mutarotation of Anilides and Substituted Anilides.

	Glucose.	Galactose.	Mannose.	Rhamnose.	Maltose.
Anilide	+10° \longrightarrow -52	-87° \longrightarrow -7	-172° \longrightarrow -82	+137° \longrightarrow +77	—
Methylated anilide ...	+224 \longrightarrow +47	-77 \longrightarrow +35	-98 \longrightarrow -39	+138 \longrightarrow +7	—
o-Carboxy- anilide ...	+87* \longrightarrow -14	-17 \longrightarrow +4	-29 \longrightarrow -21	+149 \longrightarrow +100	+49° \longrightarrow +65

* In Trans., 1909, **95**, 1555, the permanent value for this compound is given as +14.5° instead of -14.5°.

As the mutarotation of the carboxyanilides is exceedingly rapid, no special significance may be attached to the magnitudes of the

initial specific rotations, but it will be seen that the three derivatives of each sugar show mutarotation of the same order, and it would thus appear that all the above compounds are similarly constituted. It should be stated that it was only with the greatest difficulty that the above optical changes were observed, as the solutions generally attained equilibrium in a few minutes, and this suggests that other sugar complexes, at present regarded as existing in one form only, may possibly be composed of interconvertible forms.

Condensation, similar to that described, seems also to take place between sugars and certain aliphatic amino-acids, as we have succeeded in condensing glucose with α -aminopropionic acid. The product of the reaction, glucosealanide, does not display normal mutarotation, but the compound behaves in a curious manner when heated in aqueous solution. The optical activity then diminished from $[\alpha]_D^{20} + 45.7^\circ$ to the constant value 24.6° , and it was only on subsequent treatment with dilute acid that the specific rotation increased to that calculated on the assumption that one molecular proportion of glucose had been formed on hydrolysis. This result may be explained in various ways. The diminution first observed may be due to the establishment of an equilibrium between α - and β -forms of a glucosidic glucosealanide, and the subsequent rise in rotatory power to normal hydrolysis into the constituents. An equally valid explanation would be that the substance under examination was a mixture of stereoisomeric forms, which was partly hydrolysed by water and completely hydrolysed by acids. Such a mixture might contain *d*-glucose-*d*-alanide and *d*-glucose-*l*-alanide, or α -glucose-*r*-alanide and β -glucose-*r*-alanide. In all probability, the compound is a mixture of the α - and β -forms, which are interconvertible in the neighbourhood of 100° . The instability of the substance prevented further work on this question, and the sparing solubility of aliphatic amino-acids in dilute alcohol proved an obstacle in attempts to prepare other examples of this type of compound.

As a convenient method of gaining an insight into the structure of sugar derivatives is to study the corresponding alkylated compounds, we have attempted to prepare a series of condensation products from tetramethyl glucose analogous to those described in this paper and in previous publications. Unexpected difficulties were, however, encountered, in that, although unsubstituted sugars are much less reactive than alkylated sugars so far as condensation with hydroxy-compounds is concerned, the reverse holds true when the union of the condensed residues takes place through nitrogen. It seems therefore that the use of alkylated sugars in this connexion will prove of limited application.

We find that tetramethyl glucose does not give a definite condensation compound with anthranilic acid, or with alanine, and, when heated in alcoholic solution with *p*-phenetidine, β -naphthylamine, or with semicarbazide, the reaction does not proceed so smoothly as in the case of glucose. A well-defined *p*-toluidide was, however, obtained, which reacted like a glucoside towards silver oxide and methyl iodide, and showed extensive mutarotation. In sharp contrast to glucose, the alkylated sugar was not affected by ammonia or by hydrogen cyanide in the cold. Reaction proceeded in each case at higher temperatures, but in the latter instance resulted in the formation of ammonium tetramethylglucoheptonate.

Incidentally, we have made a further examination of tetramethyl glucoseoxime, with the object of ascertaining if the compound shows mutarotation. In previous work (Trans., 1908, **93**, 100) no indication of this change could be detected, although the structure assigned to the compound, on the evidence afforded by alkylation, would obviously involve the existence of two interconvertible forms. We have now succeeded in obtaining, by crystallisation, one form of the oxime giving the change $[\alpha]_D^{20} + 23^\circ \rightarrow 30^\circ$ in methyl-alcoholic solution, and, as in previous cases, the reverse optical change ($36^\circ \rightarrow 30^\circ$) was shown by the compound after fusion. The analogy between the methylated and unmethylated oximes is thus complete.

EXPERIMENTAL.

Galactose-o-carboxyanilide.

Ten grams of galactose (1 mol.) were boiled with 200 c.c. of alcohol (80 per cent.) until the sugar had passed into solution; 15 grams (2 mols.) of anthranilic acid were added, and the liquid cooled. After seventy hours, the rotation had diminished to the constant value $[\alpha]_D + 17^\circ$. The bulk of the alcohol was then removed under diminished pressure, the product separating from the concentrated solution in aggregates of small needles. The united crops were washed with dry ether and dried in a vacuum. Yield, 60 per cent.

The compound proved to be too unstable to permit of purification in bulk by recrystallisation. The only method of purification possible was to boil the substance for a considerable time with carefully purified ether, and afterwards to crystallise rapidly from ethyl alcohol. The use of more than two grams of material in the crystallisation resulted, even on spontaneous evaporation of the solvent, in the separation of some free sugar. The compound contains one molecule of combined water, which was only completely

removed by heating to $90^{\circ}/15$ mm. for several hours. Analysis of the dry residue gave:

Found, C=52.50; H=5.72; N=4.68.

$C_{13}H_{17}O_7N$ requires C=52.17; H=5.68; N=4.68 per cent.

The high carbon value found is probably due to the presence of a trace of free anthranilic acid, as the analytical figures were improved after heating the substance with a little alcohol.

The compound reacts feebly acid to litmus, and contains the carboxyl group, as a definite barium salt was obtained by neutralising a solution in 50 per cent. alcohol with barium hydroxide and precipitating with excess of alcohol. The barium content found for the dry product (Ba=19.6 per cent.) excludes the possibility of this precipitate being either barium *o*-aminobenzoate or barium galactosate, and shows the salt to be the *barium* derivative of galactose-*o*-carboxyanilide ($C_{26}H_{32}O_{14}N_2Ba$).

As the mutarotatory changes shown by the carboxyanilide are complete in a few minutes, only small concentrations may be employed, in order to limit, so far as possible, the time interval which must elapse between contact of the solvent and the first observed rotation. The initial values found thus showed considerable variation, but the permanent values were quite uniform.

Solvent: Ethyl alcohol. $c=1.1580$. *Mutarotation*, $[\alpha]_D^{20} - 17.3^{\circ} \rightarrow +4.3^{\circ}$

The compound thus exists in two interconvertible forms, and, judging from the results of a polarimetric study of the condensation carried out as described in previous papers, the *lævo*-form is the first to be produced, and is formed almost immediately.

*Mannose-*o*-carboxyanilide.*

When an alcoholic solution of mannose is boiled with anthranilic acid, partial decomposition of the acid results, and no definite product seems to be formed. The method of slow condensation in the cold proved more successful. Ten grams of the sugar (1 mol.) were dissolved in 100 c.c. of alcohol (80 per cent.), and allowed to attain constant rotation; 15 grams (2 mols.) of anthranilic acid were then added, and the solution kept at the temperature of the room. After twenty-four hours, a colourless, gelatinous precipitate separated. This was removed by filtration, and the mother liquor put aside for three months. In this way the condensation product was obtained, in nearly quantitative amount, as long, colourless needles.

The compound was easily purified by recrystallisation from absolute ethyl alcohol, separating in small needles, melting at 126° ,

from an 8 per cent. solution, and as a jelly from more concentrated solutions. Analysis showed the presence of one molecule of water:

Found, C=49·26; H=6·02; N=4·51.

$C_{13}H_{17}O_7N \cdot H_2O$ requires C=49·21; H=5·99; N=4·41 per cent.
Solvent: Methyl alcohol. $c = 2\cdot041$. Mutarotation, $[\alpha]_D^{20} - 29\cdot4^\circ \rightarrow -21\cdot1^\circ$.

Rhamnose-o-carboxyanilide.

On dissolving two molecular proportions of anthranilic acid in a 10 per cent. solution of hydrated rhamnose in 75 per cent. alcohol, a rapid fall in the dextrorotation resulted, and, after eight hours, an abundant crop of crystalline product separated. The mother liquor was worked up as in other cases, and yielded additional crops, the total yield being nearly quantitative. After purification from methyl alcohol, the compound was obtained in fine needles, melting at 167—168°. Although prepared in aqueous alcohol, and from hydrated rhamnose, the compound was anhydrous:

Found, C=55·20; H=6·26; N=4·95.

$C_{13}H_{17}O_6N$ requires C=55·08; H=6·06; N=4·94 per cent.

Rhamnose-o-carboxyanilide displays the usual solubilities and properties of these condensation compounds, but is characterised by unusually rapid mutarotation. The change is, in fact, not detectable in ethyl or methyl alcohol five minutes after the first contact of solvent and solute. Low concentrations were therefore used, and the initial values have little significance. The change is, however, much slower in pure pyridine, but even then is complete in twenty minutes:

Solvent.	Initial $[\alpha]_D^{20}$.	Final $[\alpha]_D^{20}$.	Time required to establish equilibrium.
Methyl alcohol	+66·4°	51·2°	5 minutes
Ethyl „	42·9	42·9	less than 5 minutes
Pyridine	148·8	100·2	20 minutes

Maltose-o-carboxyanilide.

The formation of this compound takes place slowly in the cold. A 7·5 per cent. solution of equilibrium maltose in 60 per cent. alcohol was mixed with slightly more than one molecular proportion of anthranilic acid, and put aside for three months. The solvent was then removed in a vacuum desiccator, and the dry, crystalline residue extracted with pure ether. The substance was so easily decomposed by solvents that it could not be further purified, but the melting point (153—155°) and microscopic examination showed the preparation to be uniform. When dried until constant in weight at 60°/15 mm., the compound contained one molecule of combined water:

Found, C=47.62; H=6.07; N=2.75.

$C_{19}H_{27}O_{12}N, H_2O$ requires C=47.60; H=6.05; N=2.92 per cent.

The mutarotation was, for this type of compound, comparatively slow.

Solvent: Methyl alcohol. $c=0.9195$. *Mutarotation*, $[\alpha]_D^{20} + 48.9^\circ \rightarrow 68.0^\circ$.

Glucosealanide.

Owing to the insolubility of alanine in alcohol, and also to the instability of the product, the preparation of this compound presented considerable difficulty. The condensation may, however, be carried out in dilute alcoholic solution either at the boiling point or in the cold, but only in the latter case can the product be obtained in the crystalline state.

A 3.5 per cent. solution of equilibrium glucose in methyl alcohol was kept at the boiling point under a condenser, and slightly more than one molecular proportion of alanine added. The acid was dissolved in water ($c=10$), and the solution introduced drop by drop from a side-tube, which was kept warm so as to avoid the formation of nuclei of the acid. The resulting solution was finally boiled for eight hours, the specific rotation, calculated on the sugar used, diminishing in this time from $+53^\circ$ to 32° . The solvent was removed in a vacuum, the residue dried at 100° , extracted with methyl alcohol, and precipitated with ether. The product was an amorphous powder, which deliquesced in air, and could not be obtained crystalline:

Found, C=43.64; H=6.82.

$C_9H_{17}O_7N$ requires C=43.03; H=6.77 per cent.

A better result was obtained by the method of slow condensation in the cold, the solution of sugar and acid being prepared as already described. After ten weeks the liquid was filtered from a trace of alanine which had separated, and evaporated in the usual manner. The residue consisted of delicate non-deliquescent needles, which softened at 110° , and melted without decomposing at 114° . No crystallising medium could be found, all attempts at purification resulting in decomposition:

Found, C=42.70; H=6.87; N=5.75.

$C_9H_{17}O_7N$ requires C=43.03; H=6.77; N=5.58 per cent.

Glucosealanide is freely soluble in alcohol or water, but no mutarotation was detected in either solvent in the cold. When an aqueous solution of the compound is heated to 90° , optical changes result, which are summarised below:

Solvent: Water. c=1.001.

Specific rotation (permanent at 20°).....	+45.7°
„ „ after two hours at 90°	+24.6°
„ „ after hydrolysis with dilute acid.....	+39.3°

The latter value, when corrected for the weight of glucose formed on hydrolysis, gives $[\alpha]_D$ 55°, so that presumably this sugar is the only active product of the change. This result is discussed in the introduction.

Nitrogen Derivatives from Tetramethyl Glucose.

As a rule, no reaction takes place between tetramethyl glucose and amino-compounds in the cold, and, at higher temperatures, the condensation is generally incomplete. Owing to solubility considerations, the separation of the unaltered sugar is difficult. The *p*-phenetidine, β -naphthylamide, and semicarbazone proved to be syrups, and, as the compounds were prepared by standard methods and no examination for mutarotation was possible, detailed description is unnecessary.

Action of Ammonia.—A 5 per cent. solution of the sugar in dry ether was saturated in the cold with dry ammonia, and after two days the solvent was removed in a vacuum. The product consisted entirely of unaltered sugar, and a duplicate experiment, in which methyl alcohol was used as solvent, also gave a negative result in the cold. On heating the latter solution at 90°, it was found that the activity diminished and became constant ($[\alpha]_D + 43^\circ$) after twenty-five hours' treatment. The solvent was removed in a vacuum, and the residual syrup extracted in the cold with light petroleum. The extract contained an oil the reactions of which corresponded with those of a condensation product, but the analytical figures obtained were not sufficiently accurate to distinguish between the aldehyde-ammonia compound and tetramethyl glucosimine.

Action of Hydrogen Cyanide.—Both ethereal and alcoholic solutions of the sugar remained unaltered in rotation when saturated with dry hydrogen cyanide and kept for several days. Experiments showed, however, that in methyl-alcoholic solution, reaction took place slowly at 90°, but after twenty hours' treatment the solution became too dark in colour to admit of further polarimetric readings. The solvent and hydrogen cyanide were removed in a vacuum, and the unaltered sugar extracted with boiling petroleum. The undissolved crystalline residue gave the reactions of an ammonium salt, and the methoxyl content found was OMe=40.47 per cent. This

result is in itself sufficient to show that the condensation is accompanied by hydrolysis, and that the compound described above is the ammonium salt of tetramethylglucoheptonic acid (Calc., OMe = 41.47 per cent.).

Tetramethyl Glucose-p-toluidide.—This compound was prepared exactly as in the case of the corresponding anilide (*loc. cit.*), heating being continued for two hours, after which the solvent and excess of the base were removed in a vacuum. The product crystallised in long prisms from light petroleum, and melted at 144°:

Found, C = 62.46; H = 8.10; OMe = 37.7.

$C_{17}H_{27}O_5N$ requires C = 62.70; H = 8.37; OMe = 38.1 per cent.

Unlike the unmethylated toluidide, the compound shows no tendency to exist in hydrated forms, and thus the examination for mutarotation was unattended by complications.

Solvent: Methyl alcohol. $c = 1.093$. *Mutarotation*, $[\alpha]_D^{20} + 156.5^\circ \rightarrow 53.5^\circ$.

The compound was recovered unaltered after prolonged heating with a large excess of silver oxide and methyl iodide, and is thus a γ -oxide. (Found, OMe = 38.8 per cent.)

Tetramethyl Glucoseoxime.—The alkylated oxime was prepared as already described (*loc. cit.*), and recrystallised several times from a mixture, in equal parts, of dry ether and low-boiling petroleum. No mutarotation was detected so long as the melting point was below 70°, but rapid crystallisation showed a continual rise in melting point until the maximum of 88° was reached. This preparation showed slight mutarotation.

Solvent: Methyl alcohol. $c = 1.50$. *Mutarotation*, $[\alpha]_D^{20} + 23.2^\circ \rightarrow 29.97^\circ$.

After fusion for one hour at 100°, the same specimen, similarly dissolved, showed the reverse change: $[\alpha]_D^{20} + 36.4^\circ \rightarrow 30.0^\circ$.

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XXI.—Cupritartrates and Analogous Compounds.

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

Tartrates.

β-Cupritartrate No. 1.—When potassium or sodium hydroxide is added to copper tartrate, the amount required to produce alkalinity is, according to Kahlenberg (*Zeitsch. physikal. Chem.*, 1895, **17**, 586), and also according to Masson and Steele (*Trans.*, 1899, **75**, 725), 1.25 to 1.27 KOH for each atom of copper. The present author obtained similar values with ordinary "pure" potassium hydroxide, but on using sodium hydroxide carefully prepared from the metal, and a well-boiled solution of copper tartrate (which is soluble to the extent of 0.015 per cent. of copper), the value obtained was 1.34NaOH (variation from 1.36 to 1.32). Phenolphthalein was used as indicator.

The product of the reaction is a deep blue solution, which, on the addition of the excess of alkali, becomes violet-blue, constituting then Fehling's solution. According to Masson and Steele, when alcohol is added to the neutral liquid, a crystalline substance separates out in the case of the sodium compound, but its composition could not be determined, owing to its decomposition on drying. The corresponding potassium compound suffers no such decomposition, but it separates as a dark blue, gummy mass: on washing this with alcohol, and drying at 100°, a very dark blue, brittle, scaly substance was obtained, to which Masson and Steele attribute the formula $K_3C_{12}H_7Cu_4O_{18} \cdot 5H_2O$. No explanation, however, was attempted of its constitution, although they showed that it contained copper in the electronegative portion of the molecule, and that potassium tartrate was one of the products of the reaction yielding it.

It is legitimate to question the purity of a substance obtained as a gummy mass, and it was found that with certain precautions it could be thrown down as a rather light blue precipitate, which, however, proved to be an emulsion; this could be collected, dissolved in water, and re-precipitated. After the first precipitation, no difficulty was experienced in obtaining it in the emulsion form, but the emulsion became finer at each precipitation, and the operation could not be repeated more than five or six times.

Two samples of the substance purified in this way gave the following values:

A.	Found : Cu = 30.36	K = 12.76 per cent.	Ratio = 3 : 2.05
B.	„ Cu = 31.24	K = 12.69 „	„ = 3 : 1.98
	Calc. : Cu = 31.01	K = 12.72 „	„ = 3 : 2.00

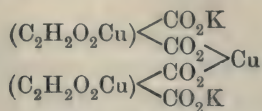
Samples less thoroughly purified contained excess of potassium, due, no doubt, to the presence of potassium tartrate, with ratios for Cu: K from 3: 2.18 down to those quoted above, but in no case was a ratio found as high as that obtained by Masson and Steele (3: 2.25).

The copper and potassium were determined, as in the case of the cupricitrates, by igniting the compound, determining the copper as oxide, and the potassium as carbonate. As the substance "scatters" on ignition, it was first decomposed by heating at a low temperature in a large closed tube, then washed into a platinum basin, evaporated, and ignited more strongly. Traces of copper always adhered obstinately to the dish, and some also passed through the filter: these were estimated separately.

A solution of the substance may be evaporated very easily, and, unlike the cupricitrates, it rapidly attains a constant weight at 100°. On heating to a higher temperature, even to 110–115°, it begins to decompose, and leaves a residue of copper oxide on dissolution.

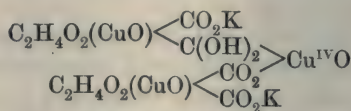
A solution evaporated until solidification begins, and left to stand, forms eventually a clear blue glass (obtained also by Masson and Steele), which contains about 9H₂O: after many months this glass becomes slightly cloudy, owing to the separation of cuprous oxide. Occasionally the substance has been obtained on evaporation in small quantities in feathery crystals, and a few crystals are also deposited sometimes on the sides of the vessel from the solution to which alcohol has been added. The dried substance, when exposed to the air, spirts in all directions, particles of it being projected to a distance of 12 or 18 inches.

The molecular proportion, copper: potassium=3: 2 agrees with that in a potassium cupritartrate with copper displacing the hydrogen atoms in the alcoholic hydroxyl groups (I); it also agrees



Mol. wt. 560.9.

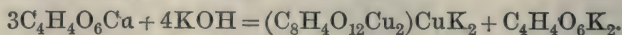
(I.)



Mol. wt. 615.0.

(II.)

exactly with the proportion of alkali which was found necessary to produce alkalinity, according to the equation:



The molecular weight, however, of such a compound is 560.9, whereas the minimum molecular weight deduced—taking the ratio Cu: K=3: 2—from the percentage of copper found is 619.1, and from the potassium 614.6, mean 616.8. Such a value agrees within

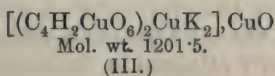
experimental error with formula II, which represents all the copper as entering the molecule by the addition of CuO, instead of the metal displacing an equivalent of hydrogen. The CuO group on the right is represented as in the cupricitrates, with quadrivalent copper; the nature and method of connexion of the other CuO groups will be discussed below.

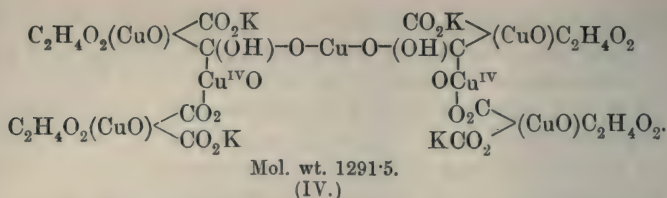
β-Cupritartrate No. 2.—When to a solution of the above cupritartrate, potassium hydroxide is added in the proportion of one molecule, or more, to each atom of copper present, and the liquid heated, it soon becomes opaque, through the separation of much cuprous and cupric oxide in a very fine state of division. If the proportion of alkali added is less than 0·3KOH, the liquid remains clear on heating, but yellow flakes of cuprous oxide separate, many of which float on the surface of the liquid. With an intermediate proportion, however, namely, 0·3 to 0·7 KOH, no cuprous oxide is formed, but the liquid, on heating, becomes deeper in colour, and a blue, gelatinous precipitate gradually separates, the whole becoming semi-solid. If alcohol, insufficient to cause precipitation, is added to the alkaline cupritartrate before heating, then, when heat is applied, the same substance is thrown down in a flocculent condition. The precipitate in either case was found to be decomposed by washing with water, and was, therefore, freed from adherent liquid by pressure in very thin layers between tiles. On drying at 100° it soon attained a constant weight, and then consisted of a violet-blue powder. On raising the temperature, slight blackening began at 110°, with a loss in weight corresponding with less than 1H₂O on the formula given below. Two samples, *A* and *B*, prepared without alcohol, and two prepared with it, *C* and *D*, gave:

* <i>A.</i>	Found: Cu=33·92	K=12·70 per cent.	Ratio=7:4·26
<i>B.</i>	„ Cu=34·77	K=12·62 „	„ =7:4·13
<i>C.</i>	„ Cu=35·04	K=12·25 „	„ =7:3·98
<i>D.</i>	„ Cu=34·54	K=12·61 „	„ =7:4·15
	Mean: Cu=34·57	K=12·54 „	„ =7:4·13
	Calc.: Cu=34·46	K=12·11 „	„ =7:4·00

* Results less certain, owing to smallness of sample.

The values for potassium would probably be high, owing to the impossibility of washing the substance; taking, therefore, the molecular ratio as being 7:4, the compound may be represented on the alcoholic hydroxyl theory by the formula III, or on the views suggested by the results with the cupritartrate No. 1, and with the cupricitrates, by the formula IV, which depicts it as a derivative from two molecules of the first cupritartrate by the substitution of an atom of copper for two of the hydroxylic hydrogen atoms:





The molecular weight deduced from the copper percentage is 1287, which agrees well with the formula IV, but is 86 units higher than that required by formula III.

The formation of this substance from No. 1 by the action of potassium hydroxide involves the formation at the same time of some other cupritartrate, similar to those described by Bullnheimer and Seitz (see below).

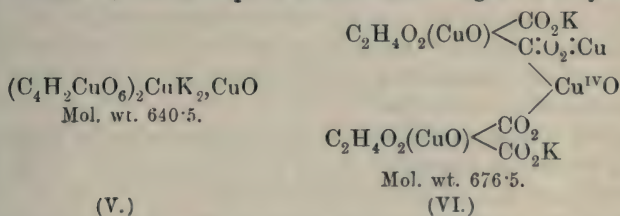
β-Cupritartrate No. 3.—When the last-mentioned compound is separated from the liquid from which it has been precipitated, and shaken with a large volume of water, it is decomposed, much copper passing into solution, and a denser violet-blue solid being left. This, in its turn, is decomposed by water, but only very gradually, the wash-water, when it is washed by decantation throughout many days, containing continuously about 0.002 per cent. of copper, after which it falls to faint traces or to nil, and the precipitate is then found to have been deprived entirely of its potassium.

The first product of the action of water, when dried at 100°, yields a violet-blue substance, which is so dark as to appear almost black before it is ground. It attains a constant weight rapidly, and loses very little further weight at 115°, when a darkening indicates that decomposition is beginning. Two samples, prepared from different preparations of No. 2, by washing until the copper contents of the filtrate became constant, gave the results *A* and *B* below. In the case of *C*, some of No. 2 was dried before being washed, and then washed on a filter with a little water, which seemed to remove at once the bulk of the soluble copper. In *D* some of the liquid containing the precipitated compound No. 2 was heated on a water-bath for three hours, and the residue collected and washed:

<i>A.</i>	Found: Cu=37.47	K=10.76 per cent.	Ratio=4:1.87
<i>B.</i>	„ Cu=37.13	K=10.53 „	„ =4:1.84
<i>C.</i>	„ Cu=37.18	K=11.47 „	„ =4:2.00
<i>D.</i>	„ Cu=37.44	K=9.98 „	„ =4:1.74
	Mean: Cu=37.31	K=10.68 „	„ =4:1.86
	Calc.: Cu=37.59	K=11.56 „	„ =4:2.00

This compound being, as mentioned above, deprived eventually of its potassium by water, the proportion of potassium formed would naturally be low, and the most probable ratio of copper: potassium is 4:2, which is actually attained in the sample *C*, when the action

of water was most restricted. Such a ratio would be given by formula VI below, representing a cupritartrate with both the carboxylic hydrogen atoms displaced by copper, and the calculated molecular weight agrees fairly well with that deduced from the percentage of copper, this giving 676·5, against 682, whereas an analogous compound represented according to the alcoholic hydroxyl theory, formula V, would require a molecular weight of only 640·5:



The relationship between the three cupritartrates is very simple, one molecule of No. 2 splitting up into molecules of Nos. 1 and 3.

Other Cupritartrates.—When the cupritartrate No. 3 is washed continuously by decantation with successive additions of water until the liquid no longer contains any potassium, two different substances are obtained according to circumstances; one of these is quite insoluble in water, is blue on drying at 100°, and gave, as a mean, Cu=43·49, H₂O (lost at 155°)=6·23 per cent., values which agree with those for an ordinary basic salt, C₄H₄O₆Cu,Cu(OH)₂, namely, Cu=43·51, H₂O=6·17 per cent. The other dissolved sufficiently in water to give a faint reaction with ferrocyanide, was of a violet-blue colour, and gave, as a mean, Cu=48·42 per cent., which agrees with the copper in a compound of a formula similar to VI above, with an atom of that metal displacing the two potassium atoms, namely, 48·02 per cent.

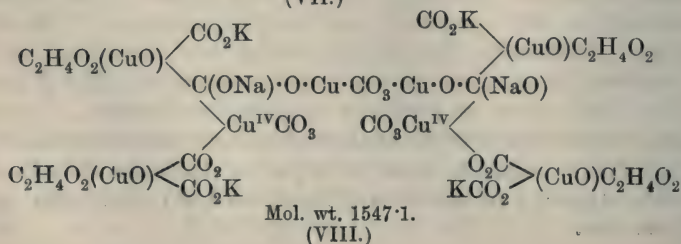
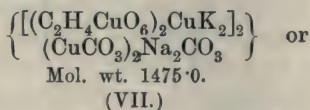
Bullnheimer and Seitz (*Ber.*, 1899, **32**, 2347; 1900, **33**, 817) obtained several tartrates and racemates which they represent on the alcoholic hydroxyl theory by the formula (C₄H₂CuO₆)M'₂ for the single salts, and (C₄H₂CuO₆)M'₂·(C₄H₂M'₂O₆)M'₂ for the double salts. These formed deeply coloured crystals, were insoluble in alcohol, and dissolved in water, giving a strongly alkaline reaction. Unfortunately the alkalinity was not determined, and its existence is inconsistent with the single salts being represented by the above formula. These salts, also, in such cases as were examined, retained one molecule of water which could not be driven off without decomposition, and which is probably constitutional water. The compounds would appear to be analogous to Luff's cupricitrate, and it is proposed to examine them in order to ascertain whether the formula suggested in that case (*Trans.*, 1910, **97**, 1844) will apply to them also.

α-Cupritartrate.—The composition of potassium *α*-cupricitrate corresponded with that of a substance consisting of two potassium cupricitrate nuclei united by a molecule of potassio-cupric carbonate; such a view received further support from the fact that potassio-cupric carbonate, although decomposed by water into a basic salt, dissolves freely in even a weak solution of potassium cupricitrate (Trans., 1910, **97**, 1845). Some carbon dioxide is given off during dissolution, owing to the simultaneous formation of another cupricitrate. A solution of potassium cupritartrate was also found to dissolve the double carbonate, but in that case no carbon dioxide was evolved.

Various circumstances appeared to complicate the results in the case of potassium cupricarbonate, which was not so in the case of the analogous sodium compound, and this salt therefore was used. Excess of it was shaken up for some time with a strong solution of potassium cupritartrate No. 1; the quantity remaining undissolved was determined by filtering, and decomposing the residue with water. It was found that rather more than twice as much of the double carbonate had dissolved as was required by the above-mentioned proportions. To the strong solution, without any of the washings from the undissolved residue, alcohol was added, and this precipitated all the copper present in the form of a light blue substance, which appeared to be partly solid and partly emulsion. The alcoholic liquid was found to be alkaline, and contained about half (Found, 53 per cent.) of the sodium carbonate in the sodio-cupric carbonate which had passed into solution; hence the carbonates must have become combined with the cupritartrate in the proportion of $2\text{CuCO}_3 : \text{Na}_2\text{CO}_3$. Analysis of the substance confirmed this. After drying at 100° , two preparations gave the mean values:

Found : Cu=32.60	K=10.07	Na=2.96 per cent.	Ratio=8 : 4.02 : 2.01
Calc. : Cu=32.87	K=10.11	Na=2.97 ,,	,, =8 : 4.00 : 2.00

This may be represented by:

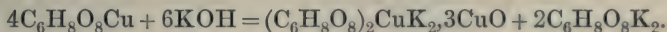


The molecular weight deduced from the copper percentage is 1560, and that from alkali metals is 1553, mean 1556, which agrees well with formula VIII. The formula VII, on the alcoholic hydroxyl theory, gives much too low a molecular weight, and, indeed, independent of this evidence against it, it is difficult to see how the constitution of such a substance can be explained on this theory at all. The alkalinity of the compound was found to correspond with the two atoms of sodium present.

When heated at 100° without previous drying, this substance appears to be partly melted and decomposed, but if dried previously over sulphuric acid, no such decomposition occurs. It then forms a light, violet-blue solid, which can be easily powdered. It begins to change in colour at 125° , and at 140° some carbon dioxide is evolved. From certain observations it seemed probable that other α -cupritartrates, that is, cupritartrates containing carbonate, existed, especially when the carbonate used was that of potassium.

Saccharates.

β -Cuprisaccharate.—Copper saccharate, prepared by double decomposition,* and having the composition $C_6H_8O_8Cu, 2H_2O$ at 100° , requires $1.49KOH$ to become alkaline, indicating the formation of a compound analogous to the cupritartrate No. 3 (p. 173):



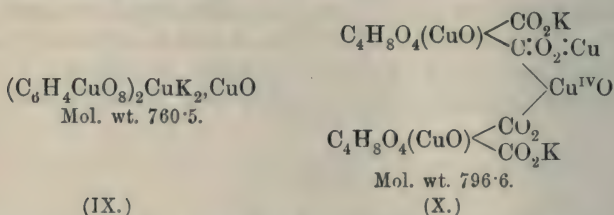
On adding alcohol to the blue solution thus obtained, a bulky, light blue precipitate was formed, which, when dried at 100° , appeared almost black, although it showed a violet-blue colour when ground. On dissolving it in water, and reprecipitating it, it became darker and more transparent at each precipitation, and finally it was so transparent that no precipitate could be recognised as present until the liquid was filtered.

Analyses of one preparation after four successive precipitations are given below (*A* to *D*), and indicate that excess of potassium hydroxide is present at first. In a second preparation a deficiency of alcohol was added for the first precipitation, and in that case the composition of the precipitate remained unaltered by repeated dissolution and precipitation (*E* and *F*), agreeing with that of the product ultimately obtained in the first preparation:

* If a solution of it containing potassium sulphate is evaporated, a sulpho-saccharate, which is freely soluble, is formed. Potassium hydroxide converts this into what is apparently a potassium cupri-sulphosaccharate.

{	A.	Found : Cu=25·27	K=12·89 per cent.	Ratio=4 : 3·32
	B.	Cu=27·99	K=12·46 "	" =4 : 2·89
	C.	" Cu=30·67	K=10·59 "	" =4 : 2·24
	D.	" Cu=31·57	K=10·08 "	" =4 : 2·08
	E.	" Cu=31·54	K=10·02 "	" =4 : 2·06
{	F.	" Cu=31·68	K=10·07 "	" =4 : 2·07
	Mean :	Cu=31·60	K=10·06 "	" =4 : 2·07
	Theory :	Cu=31·92	K= 9·82 "	" =4 : 2·00

The ratio of the potassium to copper is somewhat high, but leaves little doubt that it should be 2 : 4, as indicated by the amount of potassium hydroxide required for the formation of the substance. The copper leads to a molecular weight of 804·7, and the potassium to 777·3, the mean of which, 791, agrees fairly well with the formula X, analogous to that of the cupritartrate No. 3:



The temperature at which this salt was dried was 125°; when heated to a higher temperature decomposition begins, although with very little further loss in weight. On ignition, it swells up to a great bulk, but decomposes quietly. The anhydrous salt exhibits the same peculiarity as the β -cupritartrate No. 1, of scattering when exposed to air.

A weak solution of it gives no trace of red with ferrocyanide, however long it is kept, but if the solution is boiled, and then cooled, before the ferrocyanide is added, a portion of the copper in it reacts, but only very slowly. After being kept in the cold for two days, the whole of the copper in the boiled solution again becomes inert. With a strong solution of the substance, ferrocyanide gives an almost black liquid, from which a brown precipitate separates after some hours.

Mucates.

β -Cuprimucate.—Copper mucate, prepared by double decomposition, retains 4H₂O at 100°, and becomes anhydrous at 120°. It dissolves in water to the extent of only 0·00008 per cent. of copper. When potassium hydroxide is added to it, it dissolves slowly to form a deep blue solution, the proportion required before alkalinity is reached being 1·59KOH for each atom of copper present, indicating a reaction similar to that occurring in the case of the saccharate. The solution obtained, unless very dilute, turns in a few minutes to a jelly; it is only when the copper percentage is

about 0.5, or less, that the solution, even when hot, can be filtered. It may be boiled without decomposition.

The addition of alcohol to it throws down a bulky, gelatinous precipitate, which, on re-dissolution in water and reprecipitation, becomes more transparent at each operation, as in the case of the cuprisaccharate. On drying, the precipitate forms a dark violet-blue powder, which suffers no decomposition until about 135° . The samples analysed were dried, therefore, at 120° . The results were similar to those with the cuprisaccharate; the ratio of Cu : K was as high as 4 : 3 or 4 : 2.5 after one precipitation, but fell and became constant after two or, sometimes, three precipitations. Two samples were also prepared without the addition of alcohol, by allowing the solution to gelatinise, and working the jelly on a tile until it was deprived of its moisture. The mean results with four specimens gave:

Found : Cu = 31.82	K = 9.61 per cent.	Ratio = 4 : 1.96
Calc. : Cu = 31.92	K = 9.82 ,,	,, = 4 : 2.00

The possible formulæ will be the same as those for the saccharate (p. 176), and the molecular weight calculated for the second of them, 796.6, agrees fairly well with that deduced from the above analyses, the copper giving 799.1, and the potassium, 813.7; mean, 806.4.

Potassium cuprimucate is a colloid, and its ready gelatinisation is in accordance with the known behaviour of colloids; but it exhibits a reversal of this change, which has not been noticed in other cases. When the jelly, which must not be too strong, is filtered under pressure, it passes completely through the paper, forming what appears to be a perfect solution, except that it is always slightly cloudy; this solution gelatinises again after a day or two. A similar change may be brought about by merely shaking the jelly, it being thereby converted into a solution. That the difference between the jelly and solution is not one in appearance only may be seen by placing some of each on a porous tile, when the solution is entirely absorbed, whilst the jelly is gradually deprived of its water, leaving a solid residue behind. As the jelly doubtless consists of aggregates of molecules, the change here noticed must be regarded as an instance of chemical combination, being broken down by such simple mechanical means as pressure or shock.

The cuprimucate, unlike the cuprisaccharate, always seems to react with ferrocyanide, but only very slowly.

Cupriquinates.

Although the compounds obtained from quinic acid have not afforded additional evidence as to molecular weight of these cupri-

compounds, they may be mentioned in connexion with those from the other tetrahydroxy-acids.

Copper quinate, prepared by boiling copper hydroxide or carbonate with quinic acid, and precipitating by alcohol, is a crystalline basic salt, $[\text{C}_6\text{H}_7(\text{OH})_4\text{CO}_2]_2\text{Cu}, \text{CuO}$, which contains $8\text{H}_2\text{O}$ after drying at 100° , and dissolves in water to the extent of 0.02 per cent. of copper. Prolonged boiling of the acid with excess of carbonate results in the formation of a dark green, more highly basic quinate.

The addition of potassium hydroxide to copper quinate gives a solution which gelatinises after a few minutes, and cannot be filtered unless the copper content is less than 0.2 per cent. The cupriquate thus resembles the cuprimucate, except as regards colour, and, also, that, when once it has been well boiled, it does not re-gelatinise. It seems impossible in this case to determine the exact point at which alkalinity appears on the addition of potassium hydroxide, the colour changes (with phenolphthalein as indicator) are uncertain, and the alkali required seems to vary with the dilution; various determinations gave from 0.67 to 1.0 KOH for each atom of copper. Excess of alkali gives a blue liquid. The precipitate obtained on adding alcohol to the neutral solution was also found to vary in composition, and likewise to vary rapidly in some cases when re-dissolved and reprecipitated. Two preparations thus treated and dried at 125° , which was the highest temperature which the substance would bear without decomposition, gave:

A	1st Ppt. :	Cu=33.82	K=9.45 per cent.	Ratio=2 : 0.91
	2nd ,,	Cu=35.16	K=7.52 ,,	,, =2 : 0.70
	3rd ,,	Cu=36.63	K=6.21 ,,	,, =2 : 0.55
B	1st ,,	Cu=34.94	K=3.33 ,,	,, =2 : 0.16
	2nd ,,	Cu=34.92	K=3.25 ,,	,, =2 : 0.15
	3rd ,,	Cu=34.99	K=2.68 ,,	,, =2 : 0.13

The first preparation approached in composition to a potassium cupriquate with two CuO groups, $\text{CO}_2\text{K} \cdot \text{C}_6\text{H}_7(\text{OH})_4 \cdot 2\text{CuO}$ (analogous to the cupritartrate, etc.), containing $\text{CuO}=32.66$ and $\text{K}=10.04$ per cent., the change on repeated precipitation consisting (as in the case of the cupritartrate) in the formation of some copper cupriquate, which contains 41.71 per cent. CuO . The second preparation, however, is not amenable to such an explanation, and must contain some other cupri-compound.

Indefinite results of this character have, so far, been obtained in the case of several other monobasic acids which have been examined.

The cupriquate requires the addition of a large volume of alcohol for its precipitation, and the precipitate, especially in the case of the second of the above preparations, was extraordinarily fine and transparent; the liquid remained quite clear and limpid, and passed through filter paper without leaving the slightest

residue; it was only when filtered through a Berkefeld filter that precipitation was found to have occurred, scarcely a trace of copper remaining in solution. When a solution of it is evaporated to a small bulk and left over sulphuric acid, it dries to a transparent, green, brittle glass, resembling the hydrated cupritartrate; after a time this becomes alkaline and opaque, copper oxide separating.

Conclusion.

The results detailed above can leave very little doubt that these cupri-compounds must be considered as substances in which CuO is added to the nucleus, and not as substances in which copper atoms displace hydrogen atoms, this applying to the hydrogen in the carboxyl groups, as well as to that in the alcoholic groups. The percentage errors between the found and calculated molecular weights on these two views are:

		Copper substituted for hydrogen.	CuO groups added to molecule.
β -Cupritartrate	No. 1	+10.0 per cent.	+0.3 per cent.
"	No. 2	+7.0 "	-0.3 "
"	No. 3	+7.0 "	+0.8 "
α -Cupritartrate	+5.5 "	+0.6 "
β -Cuprisaccharate	+4.0 "	-0.7 "
β -Cuprimucate	+6.0 "	+1.2 "

The difference between the two sets of formulæ is in every case a question of the elements of water. With our imperfect knowledge of the nature of water of hydration, it is impossible to state confidently that water which cannot be eliminated without the decomposition of a substance is necessarily an integral part of the molecule, and, if we had to depend on an isolated instance, a determination of the molecular weight in such circumstances might be set aside; but when every one of the instances available bears the same evidence, this evidence cannot be ignored.

The nature of the CuO group in the carboxyl portion of the molecule has been discussed in previous communications, the copper being held to act as a tetrad; and it was originally suggested (Proc., 1910, 26, 17) that the CuO groups in the other portion of the molecule might be of a similar nature, with the copper atom united to two carbon atoms. Another view, which is, perhaps, less open to objection, is that the hydrogen atoms of the alcoholic hydroxyls become displaced by $(\cdot\text{Cu}^{\text{II}}\cdot\text{OH})'$ groups. This was suggested many years ago to explain the constitution of substances formed by sucrose, mannitol and dulcitol with the oxides of copper, lead, barium and calcium, of which the molecular weights—as in the present instances—preclude their being represented as compounds derived from the substitution of hydrogen by the metal. Such a

view does not preclude the possibility of hydroxylic hydrogen being displaced by copper itself under other conditions; indeed, the only explanation of Luff's alkaline cupricitrate appears to depend on a partial substitution of that sort taking place as regards one hydrogen atom (see *Trans.*, 1910, **97**, 1844), added to which, there are compounds of sucrose with the alkali metals, $C_{12}H_{21}M/O_{11}$, apparently necessitating a similar substitution, although these compounds have not been investigated sufficiently for rigorous argument. There is, however, no evidence at present for believing that a copper atom ever displaces the two hydrogen atoms in two contiguous alcoholic groups, as represented in the hitherto accepted theory as to cupri-compounds.

HARPENDEN.

XXII.—*The Reactions between Chemical Compounds and Living Muscle-Proteins.*

By VICTOR HERBERT VELEY.

EXPERIMENTS by Dr. Waller and the author on the comparative toxic effect of various classes of compounds on living muscle tissue have led to the conclusion that the results are due to chemical changes between the muscle-proteins (or their products of decomposition) and the compounds in the solutions of which the muscles are immersed (*Proc. Roy. Soc.*, 1909, *B*, **82**, 147; 1910, **82**, 206; *J. Physiol.*, 1910, **39**, 361; *Proc. physiol. Soc.*, 1908, 1909, 1910, etc.). These conclusions are based on the following arguments, stated briefly:

Firstly:—The temperature factors (namely, increase of rate of change per one degree absolute temperature) are practically identical with those previously observed for definite chemical changes; thus, the rate of increase per degree for the action of ethyl alcohol on muscle is almost identical with that of the reaction between hydrogen peroxide and hydrogen iodide (Harcourt and Esson), or of quinine with that between ferrous sulphate and chloric acid (Hood).

Secondly:—The relative reactivities of members of certain classes of compounds follow the same order (although often of a different degree of magnitude) as that observed in physico-chemical methods. Thus, the order of the paraffinoid alcohols is the same as that observed for their rates of esterification, and that of the halogen derivatives of acetic acid as their coefficients of affinity; or, again, the phenols are intermediate in their activity between the alcohols

and the carboxylic acids, precisely as the values of the heat effects of mixing equimolecular proportions of sodium hydroxide and the phenols are intermediate between those of the same base with the alcohols and carboxylic acids respectively. Examples might, of course, be multiplied.

Thirdly:—In certain cases there is evidence of a sub-division of the muscle stuff regarded as acidic and two bases, such as nicotine and quinine reacting simultaneously.

The object of the present communication is to carry the argument one step further, and to show that, in the absence of the disturbing factor of contracture, the reactions between living muscle stuff and chemical compounds can be made the subject of mathematical analysis. As the rate of reaction between *lifeless* chemical reagents is some function, generally logarithmic, and less generally linear, of time, so likewise the rate of reaction between *living* muscle stuff and a *lifeless* chemical compound follows the same general laws.

EXPERIMENTAL.

In order to make the subsequent text more intelligible, a description of the method of working, devised by Waller, is given in outline only. A sartorius muscle of a frog is dissected out and ligatured, with fine copper wires serving as conductors; the muscle is then set up in a glass vessel containing the solution (either 0.6 per cent. sodium chloride, approximately a *N*/10-solution, or that of the compound to be examined), and connected with a weighted lever recording its movements on a travelling smoked glass plate. The circuit with the secondary coil of an inductorium (Berne model) is completed on the one hand through the metal stand used to hold the glass vessel, and on the other by means of a direct wire; the primary coil is supplied by a 2-volt accumulator, and interrupted automatically every ten seconds by a clockwork relay. Independently there is also an electrically controlled clock for recording time in minutes by a lever on the same smoked plate.*

When each induction shock is passed through the muscle, there is a response or kick, which moves the recording lever; if the solution possesses a toxic action, or, according to hypothesis, enters into chemical change with the muscle stuff, then these resulting responses decrease from a maximum to nothing as the time of operation increases.

For the purpose of measurement a photograph (same size) is taken of the record, and squared millimetre tissue paper placed thereon; a curve or line is drawn of the outline of the heights of the

* In the actual experiments, parts of the apparatus, namely, vessel, muscle, and lever, were duplicated, so as to obtain simultaneous records.

responses, and of the base line or that of the lever; all irregularities due to the moment of inertia of the lever, as also those due to momentary defects of clockwork or otherwise, are thus eliminated. In other words, a smoothed curve or line is drawn.

If the heights in millimetres* of the response be taken as the measure of the chemical change between the reacting substance and the muscle stuff, representing the number of potential units of chemical change, then a graph may be drawn with the heights of these responses as ordinates, and time, in minutes, as abscissæ. A graph of this type is given in a subsequent section.

The Nature of the Chemical Changes.—The investigations of Emil Fischer and his colleagues have shown that the final products of hydrolysis of the proteins are the amino-acids of the acetic series and lactic acids, pyrrolidinecarboxylic acid, together with smaller quantities of other compounds of a similar type. Krimberg (*Zeitsch. physiol. Chem.*, 1907, **53**, 514) has obtained carnitine, the betaine of a hydroxybutyric acid, from muscle-protein.

The hypothesis can therefore be put forward that, when a muscle is immersed in the reacting solution, a partial hydrolysis of the proteins ensues, and the polypeptides thus formed subsequently react with acids, bases, or alcohols according to the equations given below, taken as simple illustrative types.

The completion of the changes, from left to right, is evidenced by an abolition of response, the formation of the products on the right-hand side producing a complete poisonous effect.

If the reacting solution be run out of the tube and saline solution substituted, then the chemical changes are reversed, and proceed from right to left, as shown by a recovery of the responses, at first small, and then subsequently increasing to their original height, less a difference due to the effect of fatigue, which will be separately discussed in the sequel.

The general equations are:

- (1) $R(NH_2 \cdot OH)_x(CO_2H)_y + xHA \rightleftharpoons R(NH_2 \cdot A)_x(CO_2H)_y + xH_2O.$
- (2) $R(NH_2 \cdot OH)_x(CO_2H)_y + yBOH \rightleftharpoons R(NH_2 \cdot OH)_x(CO_2B)_y + yH_2O.$
- (3) $R(NH_2 \cdot OH)_x(CO_2H)_y + yR'OH \rightleftharpoons R(NH_2 \cdot OH)_x(CO_2R')_y + yH_2O.$

It will, of course, be understood that in the above equations the values of x and y are supposed to be quite unknown, and that the symbol R stands for a long and complicated chain of a polypeptide type. The equations are merely intended to indicate that the acid and basic groupings of the proteins or of, more probably,

* These were measured by a graduated rule with sliding vernier; differences of 0.5 mm. being measured directly, intermediate differences taken as 0.3 mm. and 0.7 mm. as the case might be.

their initial products of decomposition are the matters involved in the chemical change.

[The phenols probably behave as acids according to equation (1), rather than as alcohols according to equation (2).]

Another view which finds favour is that the products of hydrolysis are already present in the muscle stuff on account of its moribund condition, and are not formed as an intermediate chemical change.

The difference between this view or the one given above is, of course, one of degree and not of kind.

If there are two successive chemical changes, there would probably be an induction-period from a delay occasioned by the first change; in some cases such a delay was observed, but in others, not; so there is no balance of evidence in favour of either view.

However this may be, if the interpretation of the chemical changes is correct, then the amino-acids should produce little or no effect; results given in the sequel confirm this conclusion.

The Rate of the Chemical Changes.—It was observed in the introductory section that the rate of such changes between living muscle stuff and a chemical reagent, like those between two reagents, is generally a logarithmic, less generally a linear, function of time. These two cases are discussed in the succeeding sections.

(1) *Rate of Chemical Change a Logarithmic Function of Time.*—In many cases the rate of chemical change is in accordance with a reaction of the first order (unimolecular reaction), and expressible by a general equation:

$$K = \frac{1}{t} \log \frac{r_0}{r_t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which K = factor of chemical change, t = time, r_0 = number of potential units of chemical change, or residue, when $t = 0$ and r_t = the same after time t .*

This equation is realised in the following cases amongst others:

(1) *Maleic acid*, $N/200$. Temperature 17° .

The results are set out in the following table. In column I are given the times from start (t); in column II, the number of units of potential chemical change or residue (r), measured by the heights

* This equation is more generally written $K = \frac{1}{t} \log \frac{A}{A-x}$, in which $A = r_0$ and $A - x = r_t$; the above form appears preferable to the author, as the rate of any chemical change depends on the residue at any moment of time, although in many cases for the purpose of convenience measurements are made of A , the total amount of possible change, and x , a difference after a lapse of time t .

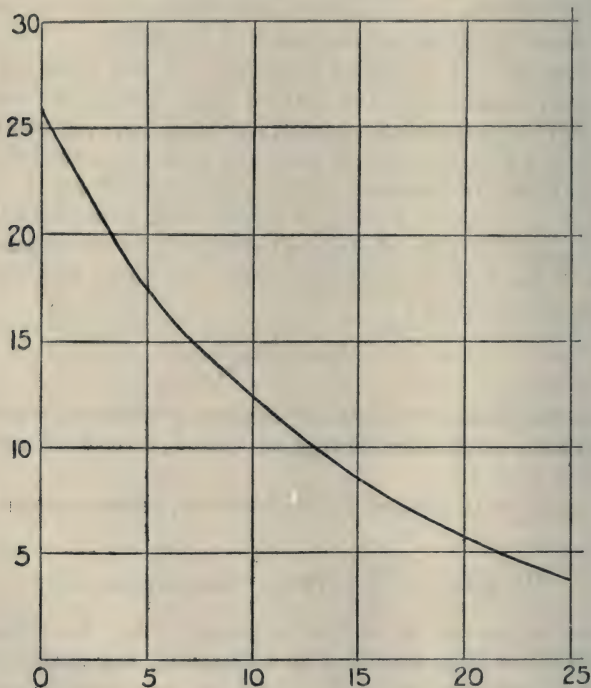
of responses; and in column III, the deduced values of K , or factor of chemical change.

(The same method will be adopted in succeeding tables without further explanation.)

TABLE I.

I.	II.	III.	I.	II.	III.
0	25.5	—	14	9.0	0.0306
2	22.0	0.0277	16	8.0	0.0309
4	18.7	0.0315	18	7.0	0.0307
6	16.0	0.0323	20	6.0	0.0309
8	14.0	0.0314	22	5.3	0.0310
10	12.5	0.0301	24	4.5	0.0310
12	10.5	0.0314			

A graph is given in the figure, the values in column II being taken as ordinates, those in column I as abscissæ.



If the first result be omitted as a low value possibly due to some induction period, the mean value of K for the remainder = 0.0311, and in the succeeding table the values of the units of potential change calculated from this datum are compared with those observed.

TABLE II.

Time.	Units calc.	Units found.	Time.	Units calc.	Units found.
4	19.0	18.7	14	9.3	9.0
6	16.5	16.0	16	8.0	8.0
8	14.3	14.0	18	7.0	7.0
10	12.3	12.5	20	6.0	6.0
12	10.7	10.5	22	5.3	5.3
			24	4.5	4.5

The agreement between the two sets of numbers is within the limits of error in the method of measurement adopted.

For the sake of comparison, a set of observations by Cain and Nicoll (Trans., 1902, **81**, 1420) on the rate of decomposition of an aqueous solution of benzenediazonium chloride, as measured by the rate of evolution of nitrogen gas, is given in table III, being presented in the same form as that of table I.

TABLE III.

I.	II.	III.	I.	II.	III.
0	58.2	—	12	24.6	0.0312
6	38.9	0.0291	17	17.2	0.0310
8	32.8	0.0311	21	13.8	0.0306
10	28.3	0.0312	30	8.5	0.0287

The mean value of K in these observations is 0.0304, which only differs by about 2 per cent. from the figure 0.0311 given above, although the first set of observations relates to a reaction between maleic acid and muscle-protein, or its hydrolysis products, and the second to the decomposition of benzenediazonium chloride.

Apart from the element nitrogen in the one case belonging to an amino-group, and in the other to the allied diazo-grouping, there is nothing in common between the two sets of changes. It is therefore reasonable to suppose that the change, which occurs when a living muscle is immersed in a dilute aqueous solution of maleic acid, is of a *chemical* nature.

(2) *Fumaric acid*, $N/200$. Temperature 19°.

Observations with this acid were made mainly with a view of ascertaining whether geometrical isomerides would show any marked difference of behaviour. The results are given below; the values calculated from the mean value of $K=0.01$ are given in column II(bis).

TABLE IV.

I.	II.	II(bis).	III.
0	17.0	—	—
2	11.0	10.7	0.094
4	6.5	6.7	0.102
6	4.2	4.3	0.101
8	2.5	2.7	0.104
10	1.5	1.5	0.094
12	1.2	1.0	0.100

The mean value of K for fumaric acid is rather more than three times than of maleic acid, which would show that the former is the more active of the two isomerides. This result is the opposite of that to be expected from physico-chemical measurements, such as electrical conductivity, rate of inversion of sucrose, etc., which give the higher value to maleic acid.

A repetition of the experiments under like conditions gave the same order for the two acids.

(3) *Acetic acid*, $N/200$.

The results obtained are given in table V, the calculated values in column II(bis) being calculated from a mean value of $K=0.0355$.

TABLE V.

I.	II.	II(bis).	III.	I.	II.	II(bis).	III.
0	17.0	—	—	14	5.5	5.7	0.0320
2	14.2	14.3	0.0340	16	5.0	4.8	0.0334
4	12.0	12.2	0.0353	18	4.2	4.0	0.0320
6	10.5	10.5	0.0334	20	3.8	3.5	0.0328
8	9.0	9.0	0.0345	22	3.2	3.0	0.0328
10	7.5	7.5	0.0351	24	2.7	2.7	0.0338
12	6.2	6.5	0.0343	26	2.3	2.5	0.0328

Although the degree of concordance is not of the fine order of accuracy to be expected in a study of a chemical reaction proceeding under fixed conditions and without disturbance of secondary changes, yet such concordance appears to be well within the limits of experimental error, having regard to the conditions of working.

(4) *Propionic acid*, $N/200$.

The results are given in the table below without further explanation. Mean value of $K=0.0138$.

TABLE VI.

I.	II.	II(bis).	III.	I.	II.	II(bis).	III.
0	15.0	—	—	12	10.0	10.2	0.0146
2	14.0	14.2	0.0150.	14	9.5	9.5	0.0141
4	13.0	13.2	0.0155	16	9.0	9.0	0.0138
6	12.2	12.4	0.0153	18	8.5	8.5	0.0137
8	11.8	11.7	0.0130	20	8.0	8.0	0.0136
10	11.0	11.0	0.0124				

In this series of results the first three observations give rather low values for heights of response, and consequently too high values of K .

As would be expected, acetic is stronger or more effective than propionic acid, the ratio of the K values being 355:138, or approximately 2.5:1. In physico-chemical methods, the ratio of

the two acids is approximately 1.3: 1, or otherwise the position of the two acids in physiological and physical methods is the same generally, but the relative order of magnitude different.

The results obtained with formic and butyric acids were identical with those of acetic acid within the limits of experimental error, although measurements by other methods have always led to a slightly higher value for the first-named.

Basic Substances.

Aconine Hydrochloride, $C_{26}H_{41}O_{11}N.HCl$; measurements by Dr. Waller with sample obtained from Dr. Wyndham Dunstan (Trans., 1894, **65**, 290). Concentration = 1 per cent., or $N/55$ (Quart. J. Exp. Physiol., 1910, **3**, 102). The results are given in the table below.

TABLE VII.

I.	II.	II(bis).	III.	I.	II.	II(bis).	III.
0	19.8	—	—	12	13.5	13.8	0.0128
2	19.0	—	0.0056	14	13.0	13.0	0.0125
4	18.0	—	0.0088	16	12.3	12.3	0.0129
6	17.0	—	0.0099	18	11.5	11.7	0.0129
8	15.5	15.5	0.0124	20	11.0	11.0	0.0125
10	14.5	14.7	0.0123	22	10.3	10.5	0.0122

The above results show clearly an induction period, in that the chemical change commences slowly, increases to a maximum, and thence decreases proportionately to the remaining units of potential chemical change.

It would not be difficult to find in chemical literature a reaction of a lifeless chemical compound proceeding on an almost identical course.

The values in column II(bis) are calculated, after conclusion of the induction period, from a mean value, $K = 0.0125$.

Dimethylaminomethyldimethylcarbinol Benzoate Hydrochloride, $OBz \cdot CMe_2 \cdot CH_2 \cdot NMe_2.HCl$, or the methyl analogue of the local anæsthetic, stovaine. Concentration, $N/500$. Temperature 17° .

The results are given below, the values in column II(bis) being calculated from a mean value of $K = 0.0450$.

TABLE VIII.

I.	II.	II(bis).	III.	I.	II.	II(bis).	III.
0	15.0	—	—	8	7.0	6.7	0.0414
2	12.0	12.2	0.0485	10	5.0	5.2	0.0478
4	10.0	9.7	0.0442	12	4.0	4.2	0.0480
6	8.5	8.0	0.0411	14	3.0	3.5	0.0435

The values in this series are rather less concordant than those of other sets of experiments; possibly this may be due to irregularities

caused by a slight separation of the free base, which can be caused even by traces of alkali dissolved out from soft glass.

Cinchonamine Hydrochloride, $N/1000$.—The results obtained with this substance (kindly supplied by Mr. D. Howard), the only poisonous alkaloid of the cinchona group, were very similar to those given in the preceding table.

Non-electrolytes.—The chemical changes which occur between muscle-proteins and substances, such as the halogen derivatives of the hydrocarbons, are somewhat difficult to interpret; further, in most cases, the muscle goes into contracture more or less rapidly, so the results cannot be made the subject of mathematical analysis.

One set of experiments obtained with a $N/100$ -chloroform solution, freshly prepared and cooled to 10° (both being necessary conditions), is given below (compare Veley and Waller, *Proc. Roy. Soc.*, 1910, *B*, **82**, 212); the values in column II(bis) are calculated from a mean value of $K=0.0298$.

TABLE IX.

I.	III.	II(bis).	III.	I.	II.	II(bis).	III.
0	18.5	—	—	12	8.5	8.2	0.0282
2	16.0	16.2	0.0315	14	7.7	7.2	0.0280
4	14.0	14.0	0.0303	16	6.5	6.2	0.0279
6	12.0	12.0	0.0313	18	5.2	5.4	0.0306
8	10.5	10.7	0.0308	20	4.5	4.7	0.0304
10	9.5	9.5	0.0290				

Other sets of experiments obtained with chemical compounds of various types might be given, but it is thought that the selection given is sufficient to establish the general principle that the reactions between chemical compounds and living muscle-proteins follow the course of reactions of the first order, and are expressible by the general equation of this type of change.

Rate of Chemical Change a Linear Function of Time.

It must be admitted that such cases do not afford such conclusive evidence as to the chemical nature of the change as those in which the rate is a logarithmic function of time, but they do not necessarily militate against the hypothesis, as certain chemical reactions do proceed as a linear function of time.

It was shown by Jones and Richardson (*Trans.*, 1902, **81**, 1146) that such changes involve the simultaneous production from one substance of at least two others, whilst the rate of formation of each of the latter is directly proportional to the amounts of the original substances present. Since the work of these chemists, Cain and Nicoll (*Trans.*, 1903, **83**, 208) and the author (*Trans.*, 1909, **95**, 1186) have studied chemical changes of this type, represented by the simple equation $K=\Delta r/\Delta t$, in which r =the number of

potential units of chemical change, t = time, and K = factor of chemical change. Suitable examples of the kind investigated are given.

Ethyl Alcohol, N/10, at 17°.

The results are given below: in column I, the times from start (t); in II, the number of units of potential change (r) expressed in the same terms as before; and in column III the values of $\Delta r/\Delta t$ or K , the factor of chemical change.

TABLE X.

I.	II.	III.	I.	II.	III.
0	19.5	—	8	7.5	1.7
2	17.0	1.3	10	4.5	1.5
4	14.0	1.5	12	1.5	1.5
6	11.0	1.5			

The figures in the third column lead to a mean value $K = 1.5 \pm 0.2$.

Trichloroethylene, N/150.—Two cases have been given in a previous paper (*Proc. Roy. Soc.*, 1910, *B*, **82**, 224), giving the same mean value for K , namely, 1.5, so that it is unnecessary to reproduce the figures. The general conclusion arrived at was that an arc of a curve had become almost coincident with the chord, or, in other words, the rate of chemical change was on a boundary line between an exponential and linear function of time.

The Effect of Fatigue.—As the view has been held that the action of a drug is nothing else than an accelerated process of fatigue, a blank experiment was conducted at a temperature of 20°, in which the muscle was immersed throughout in the salt solution. In the following table, the times are given in column I, and the heights of response in millimetres in column II.

TABLE XI.

I.	II.	I.	II.
0	17	16	13
2	17	18	12
4	17	20	11
6	16	22	11
8	16	24	10
10	15	26	10
12	14	28	10
14	14	30	9

It will be evident, on inspection of the above figures, that in the first interval of 4' there was no effect, but from this point there was a slow decline approximately as a *linear* function of time, and even after 30' the height of the response, taken as a measure of the change, was reduced by less than 50 per cent.

It must, of course, be admitted that there is a slight fatigue

effect superadded to that of the chemical compound in the experiments described above, which would tend to increase the value of the constant K (the factor of chemical change), but its effect is not of a sufficient order to interfere with the logarithmic ratio of a reaction of the first order.

It was pointed out in the text above that if the change consisted in a chemical reaction between an acid or base on amino-acids or polypeptides, then it would follow as a logical consequence that an amino-acid would produce no effect, provided, of course, that the solution was not so hypertonic as to produce a complication resulting from an osmotic effect.

The results are given in the succeeding table with a $N/25$ -solution of aminoacetic acid; the figures have the same significance as those in table XI.

TABLE XII.

I.	II.	I.	II.
0	18.0	14	13.5
2	17.0	16	12.5
4	17.0	18	12.0
6	16.0	20	11.5
8	15.0	22	11.0
10	14.5	24	10.0
12	14.0		.

On a comparison of the last two tables, it is manifest that the values in both are identical within the limits of experimental error, or, in other words, the results given in table XII are merely those of fatigue effects, and the aminoacetic acid takes no part in the matter.

A $N/10$ -solution of aminoacetic acid, namely, twenty times the concentration of the acetic acid solution examined (table V), was found to be hypertonic, and produced an osmotic effect.

In the case of other amphoteric electrolytes, the author has elsewhere (*Quart. J. Exp. Physiol.*, 1910, **3**, 237) pointed out that as the affinity value of the acid function (K_a) increases, the chemical effect likewise increases. The substances examined were tyrosine, cacodylic and aspartic acids, but other substances of the same type might also be tried.

Summary.

The main points of the present communication are as follows:

(1) When a living muscle is immersed in solutions of certain compounds, a *chemical change* takes place between the solute and the muscle-proteins or their initial hydrolysis products; its rate can be measured by the heights of response to induction shocks used as an indicating record.

(2) In most cases the rate of change is a logarithmic function of

time represented by the equation of a reaction of the first order, namely, $K = 1/t(\log r_0/r_t)$, in which r_0 is the number of units of potential chemical change when $t=0$, and r_t the number of units remaining after expiry of time t .

In a few cases, the rate of change is a linear function of time, which, although less conclusive, does not exclude the possibility of a chemical change.

(3) The effect of fatigue from induction shocks with the application of sodium chloride solution only produces a slowly diminishing result, and, as would be expected, no effect is at first apparent, and then the decrease of response is a linear function of time.

(4) If the hypothesis be correct that the chemical changes discussed under (2) are due to a reaction between the compounds, whether acid or base, and the polypeptides, either formed by hydrolysis of the muscle-protein or present by virtue of the moribund condition of the muscle, then amino-acids in not too highly concentrated solution should produce no effect. Results are given in the case of aminoacetic acid in proof of this line of argument.

In conclusion, it may be remarked that it is not to be expected that results obtained with a still living animal tissue would be of the order of accuracy of those between compounds purified with the refined art of the chemist; one comparison of these two lines of investigation show that the possible accuracy of the former is not greatly inferior to that of the latter type.

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XXIII.—*Studies of the Constitution of Soap in Solution: the Electrical Conductivity of Sodium Stearate Solutions.*

By RICHARD CHARLES BOWDEN.

THE study of the constitution of soap solutions is of the greatest importance in a large number of directions, both practical and theoretical. One of the most obvious problems still awaiting explanation arises out of the fact that there is no reason for suspecting the existence of any colloid whatsoever in solutions of sodium acetate, whilst it is equally impossible to deny the existence of

colloids in the solution of the salts of the higher homologues of this series. The question as to whether, say, sodium palmitate, $C_{16}H_{31}O_2Na$, itself is a colloid or an electrolyte is at present still entirely open, although it seems more probable that it is an electrolyte (McBain and Taylor, *Zeitsch. physikal. Chem.*, 1911, **76**, 1; *Ber.*, 1910, **43**, 321; compare Ubbelohde and Goldschmidt, *Handbuch der Chemie und Technologie der Oele und Fette*, Vol. 3).

Since the classical work of Chevreul, there are very few papers bearing directly on this problem. The boiling-point investigations of K \ddot{r} aft and his collaborators have become classical, but unfortunately the method has been shown to be quite untrustworthy (McBain and Taylor, *loc. cit.*) on account of the impossibility of removing dissolved and "sorbed" (McBain, *Phil Mag.*, 1909, [vi], **18**, 916; *Zeitsch. physikal. Chem.*, 1909, **68**, 471) air from the easily frothing, viscous solutions. Smits' vapour-tension work suffers from the same defect. The conductivity measurements of Kahlenberg and Schreiner (*Zeitsch. physikal. Chem.*, 1898, **27**, 552) in dilute solution unfortunately did not go far enough to give information about the concentrated solutions under discussion.

The investigations of McBain and Taylor have revealed some unexpectedly interesting results, in that, for example, they have shown that the equivalent conductivity of sodium palmitate passes through a pronounced maximum at a concentration of $N/2$, and a well-defined minimum at a concentration of $N/5$. Such a phenomenon has never before been met with in aqueous solution, although exactly similar cases occur in non-aqueous solutions (compare Franklin and Gibbs, *J. Amer. Chem. Soc.*, 1907, **29**, 1389).

The present paper contains measurements of the conductivity of solutions of sodium stearate, $C_{18}H_{35}O_2Na$, carried out in order to observe the effect of the addition of two CH_2 groups on the form and position of the conductivity curve. The result has been that, although, like sodium palmitate, sodium stearate is an excellent conductor at all concentrations, yet the values of its conductivity differ markedly from those of the palmitates, and the maximum and minimum of the conductivity curve have been considerably displaced.

The experimental method has been fully described in the paper of McBain and Taylor. The method is that of Kohlrausch, using telephone and induction coil. The solutions were made up and shaken until homogeneous in pure silver tubes, and they did not come into contact with the Jena-glass of the dipping electrodes until a few minutes before the actual reading. The stearic acid was recrystallised twice from absolute alcohol, and melted at 69.45° .

The "resistance capacity" of the dipping electrode was, on

account of the conductivity of the outer silver tube, a function of the observed resistance. It was measured in solutions of specially purified potassium chloride of concentration N , $N/10$, $N/50$, and $N/100$, and also in a saturated solution of specially purified sodium chloride.

The values obtained were within one per cent. of those determined a year previously by Miss Taylor. All vessels and instruments were carefully calibrated.

The work of McBain and Taylor has shown that in the case of sodium palmitate, the conductivity of a given solution is the same within the limits of experimental measurement, whether the solution is prepared by dissolving pure sodium palmitate, or by mixing sodium hydroxide solution with an equivalent amount of palmitic acid. Hence it seemed safe to make the same assumption in the case of the stearate, and to prepare the solutions by mixing pure sodium hydroxide (from sodium and conductivity water) with stearic acid. The solutions were shaken in each case for about the same length of time as the corresponding palmitates. In the following table the first column gives the weight-normality, the second the number of grams of sodium stearate in 100 grams of water, the third the capacity factor of the electrode, the fourth the specific conductivity in mhos at $90^{\circ}00'$, the fifth the density (due to E. C. V. Cornish, *Zeitsch. physikal. Chem.*, 1911, **76**, 32), the sixth the molar or equivalent conductivity at $90^{\circ}00'$, and the last the final results for the equivalent conductivity.

Sodium Stearate at $90^{\circ}00'$.

I.	II.	III.	IV.	V.	VI.	VII.
0.979	29.98	3.77	0.06326 0.06374	(0.9547)	87.98 88.65	88.33
0.4942	15.14	3.75 3.574	0.03194 0.03106 0.03115	0.9600	77.52 75.37 75.60*	76.1
0.1988	6.088	3.72	0.01398 0.01395	0.9632	77.54 77.31	77.44
0.0997	3.054	3.70	0.007105 0.007086	0.9642	76.15 75.95	76.05
0.0499	1.529	3.675	0.003680 0.003716	0.9648	77.59 78.36	77.98
0.00999	0.306	3.60	0.001208 0.001213	0.9652	125.6 126.2	125.9

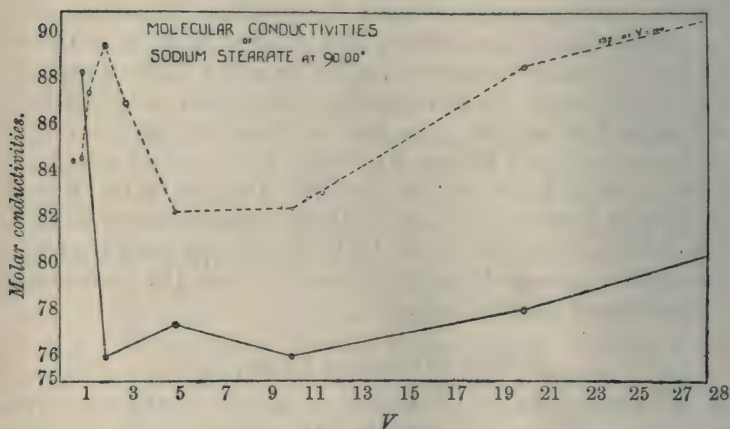
* A perfectly independent measurement made at another time by Miss Taylor.

Both the molar and the specific conductivities contain a correction of 0.1 per cent. (subtracted) on account of the thermal expansion of the electrodes.

The results are sufficiently remarkable. The conductivity remains nearly constant at the value of 77 mhos between the concentrations

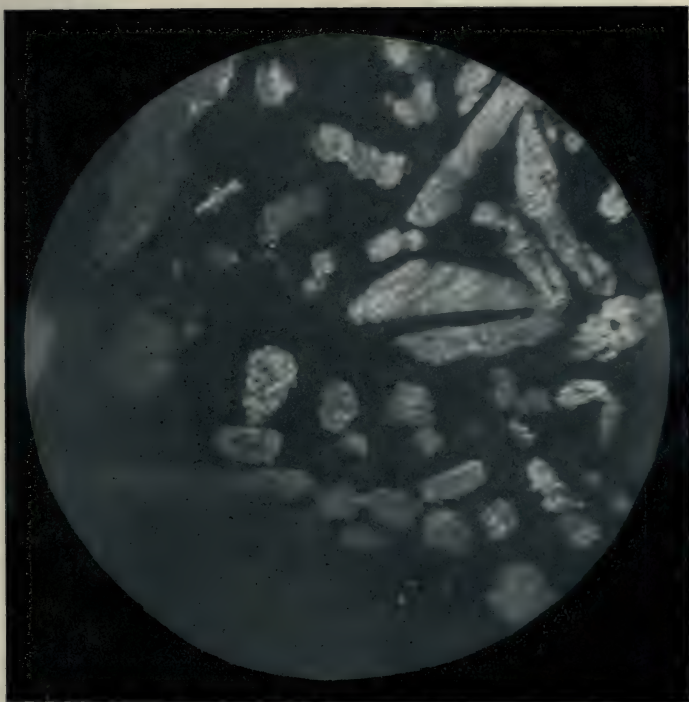
$N/2$ and $N/20$, the values then rising by 12 per cent. to 88.3 for the normal solution, and to 125.9 for the $N/100$ -solution. The figure below shows their conductivity values plotted against the volume of water in litres containing 1 gram-molecule of sodium stearate, and the values for sodium palmitate are also plotted for comparison.

In the first place, these high values obtained for the conductivity even of the most concentrated solutions prove that much electrolyte is present, and that therefore soaps cannot be simple colloids (compare Krafft and his co-workers, *Ber.*, 1894, **27**, 1747, 1755; 1895, **28**, 2566, 2573; 1896, **29**, 1328; 1899, **32**, 1584; Smits, *Zeitsch. physikal. Chem.*, 1903, **45**, 608). On the other hand, the presence of a colloid in these solutions cannot well be denied; it



seems therefore that the colloids present are the acid sodium salts, $C_{16}H_{32}O_2$, $C_{16}H_{31}O_2Na$ and $C_{18}H_{36}O_2$, $C_{18}H_{35}O_2Na$. The peculiar shape of the conductivity curve might be explained as due to the change in the degree of dispersion of the colloid. Acid sodium salt (containing an excess of sodium depending on the concentration of the free alkali in the solution) is found in dilute alkaline solution, such as the dilute soap solutions, in the form of a coagulated precipitate; it is also precipitated quantitatively (salted out) by excess of free alkali.* Intermediate solutions, such as the concentrated sodium stearate and sodium palmitate solutions, are opalescent or

* McBain and Taylor, *loc. cit.*; thus the coagulated precipitate in equilibrium with a 1.6*N*-solution of sodium hydroxide has the empirical composition of 59 per cent. $C_{16}H_{31}O_2Na$ + 41 per cent. $C_{16}H_{32}O_2$, $C_{16}H_{31}O_2Na$, as calculated from the increase in concentration of the sodium hydroxide solution employed for the salting out.



Microphotograph, No 9.

25 per cent. silver ; 75 per cent. tin, cooled in ten minutes.

Magnification = 50 diameters ; etched by HCl.

*Two elements : dark granular eutectic and light
crystalline Ag₃Sn.*



Microphotograph, No. 57.

*50 per cent. silver ; 50 per cent. tin, quenched after one hour
at 400°.*

*Magnification = 600 diameters ; etched by KCN.
Two elements : dark granular eutectic and light
crystalline Ag_3Sn .*

even quite transparent, depending on the concentration. Thus, the conductivity results might be explained by the sorptive powers of the colloidal acid salt decreasing so much as its degree of dispersion increased that the relative amount of free hydroxide in the solution increases for a time with increase of concentration. In still stronger solutions one might expect more and more of normal salt to be formed, and this, together with lessening dissociation, would explain a second decrease in the conductivity in the strongest solutions.

However, as this problem is being attacked from many different points of view in this laboratory, it would be premature as yet to regard this as being more than a plausible explanation which is in agreement with all the facts.

My sincere thanks are due to Dr. James W. McBain, at whose suggestion this work was undertaken, for his continued interest and advice.

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XXIV.—*Amalgams Containing Silver and Tin.*

By REGINALD ARTHUR JOYNER.

THE object of the present investigation was to ascertain the chemistry and physical chemistry of the ternary system—tin, silver, and mercury. Our knowledge of this system is as yet due entirely to empirical experience in dental practice * and to isolated measurements, chiefly of changes in form and of crushing strength.

Dentists have had no clue to the reasons for uncontrollable differences in behaviour of their amalgams, and hence the elucidation of the chemical changes involved appeared not only interesting from the purely scientific point of view, but fundamentally necessary for further progress in this most important branch of dental metallurgy.

Before studying the more complicated system containing the three constituents, it was obviously necessary to complete our

* Dental amalgams consist essentially of alloys of tin and silver in various proportions, amalgamated with somewhat less than their own weight of mercury. Usually several per cent. of various other metals are added in the endeavour to obtain a so-called "benevolent" effect on the amalgam, which generally takes its name from one of these slight admixtures, for example, "gold" or "platinum" amalgam.

knowledge of the three pairs of metals taken separately. Two of these systems, mercury-tin and mercury-silver, have been thoroughly and satisfactorily studied by other investigators (see p. 204). On the other hand, certain remarkable properties of the silver-tin alloys which have been discovered by dentists have never been mentioned or accounted for in chemical literature. Thus a thorough revision of previous work on these alloys was necessitated.

EXPERIMENTAL.

Great care was taken in the preparation of the metals studied, as the use of impure constituents might explain the discrepancies between the results of previous investigators. Silver chloride, prepared by dissolving silver in nitric acid and precipitating, was dissolved in ammonia, the solution filtered, and precipitated as chloride. This was fused with sodium carbonate, and the silver treated in a molten state successively with potassium nitrate, ammonium chloride, and borax, a bone ash support being employed. Best commercial tin was dissolved in hydrochloric acid; the stannous chloride which crystallised out was converted into metastannic acid by nitric acid; this was dried, and then reduced by coal gas or hydrogen in a combustion furnace. The finely divided tin thus obtained was fused under potassium cyanide and cast into bars.

Dentists have long held that the alloys of silver with tin, which constitute the essential portion of dental amalgam alloys, undergo profound changes in their properties merely through lapse of time. This phenomenon is technically called "ageing," and it is taken into account in dental practice, although not much is definitely known in regard to it.

In 1895-1897, G. V. Black published a series of researches bearing on this subject (*Dental Cosmos*, 35-39), and his results have since been given unquestioned authority. He found that fresh filings of these alloys required half as much mercury again for amalgamation as was required by similar filings which had been kept for some months, or which had been heated for half an hour to 100°. Exclusion of air did not affect these results. Again, the amalgams made from freshly prepared filings showed quite different volume changes from those exhibited by the amalgams made from "aged" filings.

Petrenko (*Zeitsch. anorg. Chem.*, 1907, 53, 200) has studied the silver-tin alloys in Tammann's laboratory, applying the modern methods of thermal analysis and of micro-photography, and his is the most important and most recent work on the alloys in question. Evidently he was unaware of the dental literature bearing on the subject, for he confined his attention chiefly to the alloys containing

a very high percentage of silver (more than 75), whilst the dental alloys contain between 40 and 70 per cent. of silver. Further, as he himself emphasised, there is an important theoretical discrepancy in his results in that the transition of β -Ag₃Sn, stable above 232°, into α -Ag₃Sn, stable below 232°, could not be detected when the alloy contained less than 50 per cent. of silver, although all the alloys lying between 35 and 75 per cent. of silver should consist, according to his results, of a mechanical mixture of pure tin with Ag₃Sn. In other words, the marked transition point of the Ag₃Sn at 232° had disappeared, whilst the alloy was still supposed to consist of Ag₃Sn to the extent of two-thirds of its weight. Thus, it seemed altogether probable that Petrenko had overlooked some compound between silver and tin lying in the region of the dental alloys. A satisfactory hypothesis could be found to explain all the facts if it were assumed that a compound such as AgSn existed and was rather slowly formed.

In the first place, the attempt was made to discover whether any alloy mixed in the proportions corresponding with Ag₂Sn, AgSn, Ag₃Sn₂, or AgSn₂ would become homogeneous and solid when kept at constant temperatures lying between 220° and 300° for several days. In no case did the alloy completely solidify above the eutectic temperature, 220°.

These experiments alone cast much doubt on the possibility of the existence of any such new compound, for the latter must have existed above 232° in order to interfere with the transition of the Ag₃Sn at this temperature.

All the alloys of tin and silver (less than 75 per cent. of silver) have been systematically investigated with regard to their micro-structure. The alloys were submitted to various treatment (quenching in water from the molten condition; annealing for days in a molten lead-bath; ordinary cooling in air, etc.), and then sections were etched by various reagents and examined in a Zeiss apparatus for metallography.

Two typical microphotographs are illustrated, facing pp. 194 and 195. The result was decisive; all the alloys containing less silver than corresponds with Ag₃Sn are unmistakably heterogeneous, no matter how prepared, or how annealed or given time to age.*

* It was noticed that almost always the alloys contained at least traces of eutectic mixture. Ignorance of this point has been fatal to the work of previous investigators; thus, Herschkowitsch (*Zeitsch. physikal. Chem.*, 1898, **27**, 125) obtained only two sets of alloys; one of these, with a low percentage of tin, had nearly the same potential as pure silver, whilst all alloys containing more than 32 per cent. by weight of tin behaved like pure tin. These results were evidently due to the actual presence of pure tin in the second set and to approximately the same isomorphous mixtures of silver and Ag₃Sn in all the alloys of the first set.

Thus the results are conclusively in support of Petrenko's view that all alloys, if well annealed, contain only the compound Ag_3Sn and free tin, no other compounds being formed in any circumstances. If, however, the alloy contains more than 50 per cent. of silver, the first solid separating out consists of a solid solution of Ag in Ag_3Sn (compare Petrenko, *loc. cit.*), the pure Ag_3Sn only becoming stable below 480° ; when the cooling is not very slow, these solid solutions are partly retained in the solid castings.

The Ageing of Filings of Alloys of Silver and Tin.

Since the after changes in the properties of the solid filings, "ageing," may take place in the cold on merely keeping the filings for some time, the phenomena might be ascribed to some metastable condition of the alloys themselves. The section above, however, has shown that only one kind of metastability can occur in the tin-silver alloys, and this only in those alloys (containing more than 50 per cent. of silver) which are not completely fused at 480° . The dental literature and Black's data in particular describe as pronounced an effect due to "ageing" in the alloys low in silver as in those containing much of that metal.

In order to confirm the existence of, and to determine the extent of, "ageing," the following method was adopted. A weighed quantity of filings, about 4 grams, was shaken with excess of mercury for exactly two minutes, and thereupon the excess of mercury was squeezed out through a small bag of chamois leather by a 56lb. weight applied through a piston in a cylinder 20 cm. in diameter. The weight was applied four times in succession, each time for thirty seconds, and it was gently rocked so that the loosely fitting piston just moved in the cylinder.

No amount of squeezing will remove all excess of mercury, but it was found that the amounts squeezed out in duplicate experiments were sufficiently constant.

In the present paper, the proportions of the silver-tin alloys are expressed in atomic percentages throughout.

If a certain amount of filings, taken immediately after filing, be treated with excess of mercury as above, a definite value is obtained for the ratio of the weight of mercury retained in the residue to the original weight of filings taken.* Thus, for example, the first two values in table I were obtained from an alloy of 60 atomic per cent. of tin and 40 atomic per cent. of silver, the ratio of mercury to alloy found being 0.78 and 0.88. Such filings, freshly prepared by filing up a cast ingot of alloy, are termed "unaged" when the

* Owing to the very low solubility of tin and silver at room temperature, the mercury squeezed out removes only a negligible amount.

filings have not been subjected to further treatment before amalgamation.

TABLE I.

Composition of alloy.	Weight taken.	Mercury retained.		Ratio mercury/alloy.
		Unaged.	Aged.	
Silver: 40 per cent.	4.37	3.42	—	0.78
" " "	4.67	4.14	—	0.88
" " "	4.47	—	1.84	0.41
" " "	4.63	—	1.89	0.41

The last two results in table I were obtained from the same filings, but these were heated for thirty minutes in an atmosphere of hydrogen at 100° before amalgamation. It is seen from the table that these "aged" filings retained only half the amount of mercury that the "unaged" filings did, namely, 0.41, instead of 0.83 of their weight.

The existence of this unique phenomenon is thus demonstrated.

It must be clearly borne in mind in the following discussion that no method of measurement or even of detection of this property is known other than that already described. When a cast bar of alloy is freshly filed, with the utmost care to avoid unnecessary force or opportunities of heating, the filings are by definition "unaged." When these filings are heated for some time at 100° they become "aged," as is seen by the relatively much smaller amount of mercury retained immediately after amalgamation.

However, after these experiments have once been carried out carefully with filings from a cast bar, more or less definite numbers are obtained for each percentage composition of the alloy which represent the two weights of retained mercury corresponding with the states "aged" and "unaged" respectively. Hence, when an amalgamation test of any alloy of a given percentage composition is compared with the two standard values representing the "aged" and "unaged" states, an extension of the above definition permits of the use of the terms, "unaged," "aged," "partly aged," in describing the alloy in question, even although the filings tested are freshly prepared from a solid bar. It will be noted that the terms apply directly only to filings, and not to the massive metal.

It will be of advantage to summarise the following results for reference in advance before discussing the experimental details.

A. The following preparations behave similarly to standard "unaged" filings: (1) Carefully filed fresh filings of all bars of cast alloy; (2) carefully filed fresh filings of all bars of "recemented" alloys containing more than 35 per cent. of silver, no matter at what temperature the "recementation" of the filings took place.

B. The following preparations were "aged": (1) All filings of alloy (not pure tin) which had been heated for an hour at 100°, with or without the exclusion of air; (2) all recemented filings from bars containing less than 25 per cent. of silver, no matter at what temperature the recementation took place; (3) many filings which were obtained by vigorous filing.

It will be readily understood that most of the filings examined were neither completely "aged" nor ideally "unaged." The unsatisfactory nature of the only method of examination available also prevented the results from possessing any high degree of accuracy; the accuracy attainable, under good conditions, hardly exceeded one unit of the first place of decimals in the ratio: mercury retained/weight of alloy.

In table II are given the standard numbers representing the "aged" and "unaged" states respectively for the various alloys. The composition of the alloy is expressed in atomic percentages of silver and tin, and also in percentage by weight of the compound Ag_3Sn . The last two columns represent the difference in weight of mercury retained by one gram of "unaged" and "aged" filings, and the ratio between these two amounts of retained mercury.

TABLE II.

Mercury Retained by "Aged" and "Unaged" Filings.

Percentage composition of alloy.		"Unaged" filings.		"Aged" filings.		Diff. in Hg, "unaged"/ "aged."	Ratio of Hg, "unaged"/ "aged."
Ag.	Ag_3Sn .	Hg alloy.	% Hg in amalgam.	Hg alloy.	% Hg in amalgam.		
*75.0	100.0	2.12	68	0.68	41	1.33	2.96
—	—	2.08	67	0.78	44	—	—
—	—	—	—	0.66	40	—	—
70.0	92.8	1.70	63	0.86	46	0.81	2.0
—	—	1.60	61	0.82	45	—	—
55.0	72.0	0.92	48	0.37	27	0.53	2.6
—	—	0.86	46	0.35	26	—	—
40.0	51.7	0.98	49	0.33	25	0.52	2.4
—	—	0.83	44	0.41	29	—	—
—	—	0.78	44	0.41	29	—	—
—	—	0.88	47	—	—	—	—
—	—	0.89	47	—	—	—	—
—	—	0.92	48	—	—	—	—
35.4	45.4	0.89	47	0.49	33	0.40	1.8
25.0	31.7	0.86	46	0.52	34	0.34	1.65
10.0	12.6	0.77	44	0.49	33	0.28	1.6
3.84	4.77	0.56	35	0.64	40	—	1.0
—	—	0.59	37	0.57	36	—	—
—	—	0.45	31	0.43	30	—	1.0

* Cooled in an electric furnace from 430—200° during a period of three days. The alloy was very slowly filed, and it was cooled under the water tap every ten seconds during filing. These values are relatively as well as absolutely the greatest which could be obtained.

Each of the following experiments was carried out in order to test a definite hypothesis in regard to the nature of "ageing," and they will therefore be dealt with in this order.

(a) Does a bar which has been heated to 100° for some time before filing yield "aged" filings?

Part of a cast bar containing 40 per cent. of silver was simply filed, whilst another part was annealed for half an hour in boiling water before filing.

Filings from cast bar gave ratio	= 0.89
„ annealed bar gave ratio ...	= 0.92

Therefore it is necessary for the alloy to be in a state of fine division in order to become "aged," but the experiment says nothing as to whether or not "ageing" is due to mechanical shock of filing (compare Cohen's "forced metals," *Zeitsch. physikal. Chem.*, 1910, **71**, 301).

(b) Do filings of tin age? The experiment gave:

Ratio for fresh filings	= 0.43
„ annealed filings	= 0.45

Thus pure tin does not age at all.

Hence in contradiction of Black's own theory, the phenomenon of "ageing" is not connected with any change from one to the other of the four known modifications of pure tin (grey, white, orthorhombic, "forced").

(c) Is "ageing" connected with a possible suspension of the transition of β -Ag₃Sn (stable above 232°) to α -Ag₃Sn (stable below 232°)?

Possibly, as Rosenhain and Tucker (*Phil. Trans.*, 1908, *A*, **209**, 89) have suggested in the case of lead-tin alloys, the tin forms a protective sheath round the metastable β -Ag₃Sn crystals.

Here, then, the act of filing might regularly convert the stable α -Ag₃Sn into metastable β -Ag₃Sn, and annealing at 100° would then restore the filings to the stable form; thus the difference between "unaged" and "aged" filings would be merely the difference in reactivity (or possibly the path of the reaction) with mercury of the metastable β -Ag₃Sn and the stable α -Ag₃Sn.

Now the alloys under consideration consist of the compound Ag₃Sn, which does not melt below 480° , with eutectic mixture, which melts at 220° , that is, 12° below the transition point. Therefore these alloys can be partly melted without any chance of the transformation taking place on re-cooling; such bars differ neither in appearance nor hardness from the original alloys. This procedure has been termed "recementation" of the filings. When a recementation experiment took place above 232° and a small piece of β -Ag₃Sn was dropped into the semi-fluid mass, every chance was

given for the conversion of the α -Ag₃Sn into the β -Ag₃Sn, particularly as in these cases the alloy was afterwards cooled quickly.

The following results were obtained, an atmosphere of hydrogen being employed in each case:

10 per cent. of Silver and 90 per cent. of Tin = 12.6 per cent. of Ag₃Sn and 87.4 per cent. of Tin.

	Ratio Hg/alloy.
"Unaged"	0.77
"Aged"	0.49
Recemented below 230° (fresh filed)	{ 0.58
	{ 0.55
" 230° and then "aged"	0.54
" above 250° (fresh filed)	0.45

The alloy recemented below 230° yielded filings which were already "aged," and practically no metastable Ag₃Sn could have been present. On the other hand, the recementation above 250°, which is the most favourable for retaining metastable β -Ag₃Sn, did not produce "unaged" filings. The latter experiment is in direct contradiction of the hypothesis (c).

25 per cent. of Silver and 75 per cent. of Tin = 31.8 per cent. of Ag₃Sn and 68.8 per cent. of Tin.

	Ratio.
"Unaged"	0.86
"Aged"	0.52
Recemented at 240–260° for one hour and fresh filed	{ 0.52
	{ 0.60
	{ 0.48

These results are likewise opposed to hypothesis (c).

35.4 per cent. of Silver and 64.6 per cent. of Tin = 45.4 per cent. of Ag₃Sn and 54.6 per cent. of Tin.

	Ratio.
"Unaged"	0.89
"Aged"	0.49
Recemented below 228° (fresh filed)	0.72
" " 227° "	0.85
" " 225° "	{ 0.78
	{ 0.79

This alloy yields "unaged" filings even when no chance has been given (except during the act of filing, and for this compare the preceding alloys) for the stable α -Ag₃Sn to turn into metastable β -Ag₃Sn. This also does not accord with hypothesis (c).

40 per cent. of Silver and 60 per cent. of Tin, or 51·7 per cent. of Ag_3Sn and 48·3 per cent. of Tin.

	Ratio.
"Unaged"	{ 0·98
"Aged"	{ 0·83
Recemented below 283° freshly filed	0·35
" " 228° "	0·74
" " 228° "	0·64

This alloy is similar to the last one.

The above results are remarkable in themselves, and do not seem to permit of explanation as yet.

(d) Is "ageing" the release by annealing of a state of strain induced by the act of filing?

The experiments with the 10 per cent. of silver and the 25 per cent. of silver alloys just cited are sufficient to disprove this, for their filings failed to produce "unaged" filings from a normally hard bar of metal.

(e) Is "ageing" a property of the Ag_3Sn contained in the alloys?

If the difference between the ratios in table II is plotted against the amount of Ag_3Sn in the alloys, a continuous curve is obtained, and when the inaccuracy of the data is borne in mind, it seems to indicate a direct proportionality between the capacity of an alloy for "ageing" and its content of Ag_3Sn . Hence the property of "ageing" seems to belong to the Ag_3Sn contained in all these alloys.

(f) Is "ageing" due to the oxidation of the Ag_3Sn particles?

When filings are heated to 100°, whether in an atmosphere of hydrogen or in air, there is a slight colour change, which becomes more marked as the content of the Ag_3Sn increases. This might be due to superficial oxidation of the tin in the compound. If, however, the surface tin were thus oxidised, silver would be left as a protective coating round each particle of "aged" Ag_3Sn . Now mercury can penetrate through half an inch of tin in a few seconds (compare Roberts-Austen, *Introduction to the Study of Metallurgy*), but it amalgamates silver only partly even after many weeks (Fenchel, *Dental Cosmos*, 1910, 52, 24). Therefore, according to the hypothesis, each particle of Ag_3Sn would be protected to some extent from the action of mercury by the silver round it.

Some 45 per cent. of silver alloy was prepared and filed, a part of the filings was "aged" and then ground in an agate mortar, whilst the other part was simply ground without "ageing":

Ratio for "unaged" pulverised	= 1·06
" " "aged" " "	= 0·42

Thus the pulverisation had not "unaged" the latter alloy, even although the pulverised filings must have offered entirely unpro-

tected fresh surfaces for the action of mercury. This renders hypothesis (f) untenable.

To sum up, "ageing" is a property of the Ag_3Sn contained in the alloys, and a state of fine division is essential for its occurrence; pulverising "aged" filings does not "unage" them. Probably electromotive force measurements would throw light on the phenomena. It seems as if the only possible explanation left is that "ageing" is due to polymerisation of the Ag_3Sn (compare the relationships found by Allmand in the case of copper hydroxide, *Trans.*, 1909, **95**, 251; 1910, **97**, 603).

It will be seen below that "ageing" does not affect the nature of the amalgam finally obtained, provided that excess of mercury is present.

It was found that no more mercury is taken up either by "aged" or "unaged" filings after a few days, and the final proportion of mercury retained in the solid is the same in both cases; this, in confirmation of the results of the solubility measurements to be described, shows that the solid amalgams ultimately obtained from "aged" filings are identical with those made from "unaged" filings.

Thus the sole effect of "ageing" is to retard the initial stages of amalgamation.

Tin Amalgam.

Tin amalgam has been most thoroughly studied by W. J. van Heteren (*Zeitsch. anorg. Chem.*, 1904, **42**, 129). He determined the melting points of all amalgams from pure tin to 5 atomic per cent. of tin, which melted at 65° .

The following table contains all his analyses of the liquid phase together with some further determinations:

Temperature.	Tin in liquid phase.	
	van Heteren.	Joyner.
-18.8°	0.36 atomic per cent.	—
0.0	0.59 " "	—
14.0	—	1.05 atomic per cent.
15.0	0.97 " "	—
25.0	1.21 " "	—
25.4	—	1.24 " "
63.2	—	4.04 " "
90.0	—	18.0 " "
163.0	—	66.7 " "

From electromotive force experiments, he concluded that no compound between tin and mercury exists, but solid tin amalgam is simply mixed crystals containing about 1 per cent. of mercury.

Silver Amalgam.

The constitution of the silver amalgams at the ordinary temperature has been finally established by the thorough investigation of Ogg (*Zeitsch. physikal. Chem.*, 1898, **27**, 285) and Reinders (*ibid.*, 1904, **54**, 609). Only the compounds Ag_3Hg_4 , Ag_3Hg_2 , and Ag_3Hg can exist, and of these Ag_3Hg_4 , commonly called "Arbor Dianæ," is the only one readily formed.

The following determinations of the composition of the liquid phase in equilibrium with the compound Ag_3Hg_4 have been made:

Temperature.	Atomic per cent. of silver in liquid phase.
14°	0.07
25	0.082
30	0.086
63	0.19
90	0.34
163	1.13

Reinders obtained 0.076 atomic per cent. at room temperature.

The Ternary System: Tin, Silver, Mercury.

Chemical literature contains no data at all in regard to the alloys of mercury with silver and tin. The solid amalgam used for dental fillings are usually made by filing up the silver-tin alloy, rubbing it with mercury in the hand or in a mortar, and squeezing out some of the excess of mercury. The pasty, semi-crystallised solid so obtained hardens within the course of a few hours or days, although very slight changes of form and possibly of volume continue to take place for many months or years. This hardening is obviously due to chemical change, although it has been hitherto unexplained. The experiments which follow demonstrate conclusively that the chemical reaction results in the breaking up of the compound between the tin and the silver (Ag_3Sn) in order to form the compound Ag_3Hg_4 , leaving all the tin in the free state. As will be seen, other relationships hold at higher temperatures.

A comprehensive series of cooling curves of the various amalgams were taken, but the chemical changes involved are too slow for this method to be advantageous. It was found that all amalgams of tin and silver, even those that have long hardened, undergo partial fusion at 65–100°, and gradually become more completely fluid as the temperature is raised. No break in the cooling curves is met with at higher temperatures. This means that there are only two groups of equilibria corresponding with higher and lower temperatures respectively.

Investigation by Analysis of the Liquid Phase.

The phase rule predicts that the solubility of a given component in the liquid phase must remain constant so long as any of this component exists free as a pure solid phase. A sudden break in the concentration in the liquid phase will thus occur when one of the two solid phases allowed by the phase rule disappears and is replaced by another. Should no compound exist containing both silver and tin in combination with mercury, the composition of the liquid amalgam is constant independent of the relative proportions of the metal in the solid phase. This simplest case is realised in the present system at room temperatures.

The following procedure was finally adopted. An alloy of definite proportions was prepared, filled, and placed in a glass tube, and on the tube being filled with hydrogen, mercury in excess was added, and the tube sealed off. The tube was then placed in a thermostat, and was frequently shaken. It was found that equilibrium is attained in about a week, but a fortnight was allowed. For analysis the tube was opened, and by means of a glass tube with a plug of glass-wool in the end, a quantity of the liquid phase, free from solid, was withdrawn by means of a pipette. This was weighed, dissolved in 100 c.c. of nitric acid (1.4), and the solution boiled for a minute or two, this being necessary to convert the mercurous nitrate into the mercuric salt. After the evolution of brown fumes had ceased, water was added (200 c.c.), and the solution again brought to the boiling point and then allowed to settle. The metastannic acid thus formed was collected and estimated in the usual way. To the filtrate, the calculated amount of ammonium chloride necessary to convert all the mercuric nitrate to mercuric chloride was added. The above precautions are necessary, since silver chloride is soluble in solutions of mercuric nitrate (Trans., 1908, **93**, 1405), and is therefore not completely precipitated as long as any of the latter salt remains. To free the silver chloride, which was formed in a very finely divided condition, from small amounts of calomel, the precipitate was treated with ammonia solution, the silver being reprecipitated by nitric acid. The silver chloride was then estimated in the usual way.

In all the experiments described, the amount of solid alloy added to the mercury was at least double the amount necessary to saturate the mercury with tin.

The following experiments were carried out with "aged" filings at $25.40^{\circ} \pm 0.01^{\circ}$.

TABLE III.

Alloy.	Percentage of tin in liquid amalgam.	Percentage of silver in liquid amalgam.
100 per cent. of tin	0.743	—
90 " "	0.751	—
80 " "	0.750	—
70 " "	0.760	0.045
60 " "	0.743	0.046
50 " "	0.748	0.048
40 " "	0.762	0.050
30 " "	0.751	0.040
20 " "	0.743	—
10 " "	0.752	—
0 " "	—	0.043
Average	0.751	0.045

A repetition of the above experiments, using double the amount of "aged" filings for the same amount of mercury, gave the following results (there was not enough liquid phase for analysis in the experiments, using 10 and 20 per cent. of tin):

TABLE IV.

Alloy.	Percentage of tin in liquid amalgam.	Percentage of silver in liquid amalgam.
50 per cent. of tin	0.751	0.043
40 " "	0.755	0.040
65 " "	0.748	0.046
70 " "	0.756	0.044
Average	0.753	0.043

Finally, the following experiments with "unaged" filings were carried out, but at $25.6^{\circ} \pm 0.01^{\circ}$:

TABLE V.

Alloy.	Percentage of tin in liquid amalgam.	Percentage of silver in liquid amalgam.
20 per cent. of tin	0.750	0.033
60 " "	0.760	0.044
78 " "	0.764	—
Average	0.758	0.041

These striking tables demonstrate conclusively that at room temperature no solid amalgam exists containing both silver and tin. The silver amalgam, which has the composition Ag_3Hg_4 (Reinders and Ogg, *loc. cit.*), exists quite independently of the solid tin amalgam, which is a solid solution of a per cent. or so of mercury in tin. Again, the solid amalgams, formed from the "aged" filings, are identical with those obtained from "unaged" filings, since the analyses of the saturated liquid

amalgams do not differ by more than 0·8 per cent. of the 0·75 per cent. of tin present.

Similar experiments were carried out at $63\cdot05^{\circ} \pm 0\cdot15^{\circ}$ with the following results:

TABLE VI.

Alloy	Percentage of tin in liquid amalgam.	Percentage of silver in liquid amalgam.
0 per cent. of silver	2·35	—
0 " "	2·36	—
*0 " "	2·36	—
0 " "	2·34	—
*20 " "	2·58	0·184
*30 " "	2·52	0·177
*50 " "	2·56	0·185
60 " "	2·60	0·184
80 " "	2·56	0·175
100 " "	—	0·100
" " "	—	0·103

Cohen and Inouye (*Zeitsch. physikal. Chem.*, 1910, **71**, 626), in a recent paper on zinc amalgam, have emphasised the magnitude of the inaccuracy possible in such solubility determinations at higher temperatures. Hence in the measurements marked with an asterisk a filter of chamois leather attached to a suction pump was employed for drawing off the liquid amalgam for analysis. It is satisfactory to note that this made no difference in the results.

It is evident that at 63° the only two solid phases occurring are still the compound Ag_3Hg_4 and the solid solution of mercury in tin. The solubility curve of solutions saturated with respect to both mercury and tin forms a very flat curve through the three known points, and thus measurements at intermediate temperatures have been unnecessary.

Thus the general form of the ternary diagram is established for the temperatures from the melting point of mercury up to 63° .

There is no eutectic mixture, since the solubility of tin and of silver both become immeasurably small well above the solidification point of mercury.

The simple relationships which have been found for temperatures up to 63° do not hold at higher temperatures. There is a sharp transition point near 70° with the formation of a ternary compound, possibly $(\text{Ag}_3\text{Sn})_2\text{Hg}$; this will form the subject of a further communication.

In conclusion, I wish to express my sincere thanks to Dr. James W. McBain for the very kind help he has given me in my work, which was undertaken at his suggestion.

XXV.—*Additive Compounds of Phenols and Phenolic Ethers with Aromatic Polynitro-derivatives.*

By JOHN JOSEPH SUDBOROUGH and STANLEY HOSKINGS BEARD.

ATTENTION has already been drawn to the readiness with which arylamines combine with aromatic polynitro-compounds (Trans., 1901, **79**, 522; 1903, **83**, 1334; 1906, **89**, 583; 1910, **97**, 773), and it has been shown that the effects produced on the colour of the additive compound by the introduction of substituents into the arylamine molecule are exactly parallel to the effects produced by the same substituents on the auxochromic nature of the primary amino-group. It is well known that the hydroxyl group is an auxochrome, although not so powerful as the amino-group. We were therefore induced to determine whether phenols and their derivatives are also capable of forming coloured additive compounds with trinitrobenzene and similar polynitro-derivatives.

The results show that such coloured additive compounds can exist, but that as a rule the colours of the compounds are not so pronounced as in the case of the additive compounds with arylamines. This is well shown by a comparison of the additive compounds which trinitrobenzene forms with the naphthylamines and naphthols:

α -Naphthylamine and trinitrobenzene.....	Brick-red.
β -Naphthylamine " " 	Deep brick-red.
α -Naphthol " " 	Orange-yellow.
β -Naphthol " " 	Canary-yellow.

Compounds of phenols with trinitrobenzene do not appear to have been prepared previously, but numerous examples of additive compounds of picric acid with phenols and phenolic ethers have been described, and recently Meldola (Proc., 1908, **24**, 210) has prepared a stable red additive compound of β -naphthol with trinitroacetylaminophenol.

In our experiments with amines we were able to show that combination with trinitrobenzene takes place when the nitrogen atom of the imino-group forms part of a closed ring, for example, triphenylpyridine, tetrahydroquinoline, etc. We also find that when the oxygen atom forms part of a ring the compound is capable of combining with trinitrobenzene. The best example to illustrate this point is coumarone, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CH} \\ \diagdown \text{O} \end{array} \text{CH}$, which yields a very pale yellow, crystalline, additive compound. Diphenylene oxide, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{array}$, also forms a definite additive compound.

Ketones, for example, benzophenone, acetophenone, benzoin, benzil, and deoxybenzoin do not appear to form additive compounds, and when both CO and O groups are present in a ring system, for example, xanthone, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix} C_6H_4$, and dimethylpyrone,

$CO \begin{smallmatrix} \diagup CH:CM_e \\ \diagdown CH:CM_e \end{smallmatrix} O$, additive compounds with trinitrobenzene are not formed; in the case of coumarin, the formation of an additive compound is shown by an examination of the melting-point curve.

The various phenolic ethers also tend to form coloured additive compounds with trinitrobenzene; the colours of these compounds are, as a rule, yellow, but quinol dimethyl ether forms an orange-red additive compound, and asarone a deep prune-coloured compound. As regards colour, there is no marked difference between the compounds derived from the phenols and those derived from their ethers. Similarly, Hofmann points out that the auxochromic effects of the hydroxyl and methoxyl groups are very similar.

In a former communication (*loc. cit.*, p. 776) we have drawn attention to the fact that quinoline and substituted quinolines form nearly colourless additive compounds with trinitrobenzene. Our present results show that by the introduction of a hydroxyl group into the quinoline molecule, more stable and more deeply coloured additive compounds are formed with trinitrobenzene. The colour of the additive compounds is, as a rule, canary-yellow when the hydroxyl group is attached to the pyridine nucleus, but of a brown or brownish-green colour when the hydroxyl group is attached to the benzene nucleus.

A comparison of the behaviour of the isomeric pairs of compounds:

Eugenyl methyl ether.	<i>iso</i> Eugenyl methyl ether.
Safrole.	<i>iso</i> Safrole.
Apiole.	<i>iso</i> Apiole.

towards trinitrobenzene was of interest, as Bruni and Tornani (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 184) state that the compounds containing a propenyl group ($\cdot CH:CHMe$) form additive compounds with picric acid, whereas the isomerides containing an allyl group ($\cdot CH_2 \cdot CH:CH_2$) do not form such compounds.

Our experiments prove that apiole and safrole and also *iso*apiole and *isosafrole* form additive compounds with trinitrobenzene. These compounds are comparatively stable, and can be crystallised from solvents. It is noticeable, however, that the colour of the compounds containing a propylene group are more pronounced than those containing an allylene group; thus, *isoeugenol*, *isoeugenyl* methyl ether, *isosafrole*, and *iso*apiole all yield brilliant red additive compounds, and asarone yields a prune-coloured compound with

trinitrobenzene. The colours of the additive compounds are undoubtedly influenced by unsaturated linkings or subsidiary latent valencies in groups adjacent to the benzene nucleus. Thus, amines with the tervalent nitrogen atom (two latent valencies) directly attached to the benzene nucleus form deeply coloured additive compounds, phenols and phenolic ethers with the bivalent oxygen atom (two latent valencies) attached to the nucleus form less deeply coloured products, and compounds which possess phenolic oxygen and a propenyl side-chain both attached to the nucleus give deep red-coloured compounds.

The fact that cyclic compounds containing both a carbonyl group and a bivalent oxygen atom in the ring do not readily form additive compounds with trinitrobenzene may be due to the fact that the latent valencies of the oxygen atom are neutralised by the carbonyl in a manner similar to that suggested by Collie in dimethylpyrone.

We have previously pointed out (Trans., 1910, **97**, 777) that compounds containing both hydroxyl and amino-groups do not form stable additive compounds with trinitrobenzene. We have not been able to confirm this by the examination of freezing-point curves, as mixtures of trinitrobenzene and an aminophenol decompose when heated. It is possible that the inability to form stable additive compounds may also be due to the fact that the subsidiary valencies of the oxygen and nitrogen atoms neutralise one another. This is supported by the readiness with which amines form additive compounds with phenols (compare Dale and Schorlemmer, Trans., 1883, **43**, 185; Dyson, *ibid.*, 466; Hebebrand, *Ber.*, 1882, **15**, 1974; Philip, Trans., 1903, **83**, 814; Philip and Smith, *ibid.*, 1905, **87**, 1735; Kremann, *Monatsh.*, 1906, **27**, 91; Dollinger, *ibid.*, 1910, **31**, 643; Schmidt and Wichmann, *Ber.*, 1891, **24**, 3237; Stevignon, *Bull. Soc. chim.*, 1910, [iv], **7**, 922), as do also phenols and ketones (Schmidlin and Lang, *Ber.*, 1910, **43**, 2806), and amines and quinones (Loring Jackson and Clarke, *Amer. Chem. J.*, 1905, **34**, 441).

Aromatic hydrocarbons also form additive compounds with trinitrobenzene. We have already prepared a number of these additive compounds. That formed by naphthalene and trinitrobenzene crystallises in light yellow-coloured needles, and the introduction of the hydroxyl group tends to deepen the colour of the additive compound. Other substituted derivatives of naphthalene also yield compounds with trinitrobenzene; thus, methyl α -naphthoate and methyl β -naphthoate form stable additive compounds, which crystallise from alcohol in very pale yellow needles.

A few additive compounds of phenols with polynitro-derivatives of naphthalene, namely, α -tri- and β -tetra-nitronaphthalene, have

EXPERIMENTAL.

The following table shows the properties of the compounds prepared:

I.—*Additive Compounds of Phenols with Aromatic Polynitro-derivatives.*

Components.	Mols. of nitro- compound: mols. of phenol.	Formula.	Appearance.	M. p.	Analysis.	
					Found, per cent.	Calc., per cent.
α -Naphthol and <i>s</i> -trinitro- benzene	1 : 1	$C_{16}H_{11}O_7N_3$	Orange-yellow needles	178–179°	N = 11.97	11.77
* β -Naphthol and <i>s</i> -trinitro- benzene	1 : 1	$C_{16}H_{11}O_7N_3$	{ Canary-yellow needles (alcohol) } { Orange-yellow needles (benzene) }	158–158.5°	N = 11.65	11.77
Phenyl salicylate and <i>s</i> -tri- nitrobenzene	1 : 1	$C_{19}H_{13}O_9N_3$	Pale yellow needles	85°	N = 10.02	9.84
Benzyl salicylate and <i>s</i> -tri- nitrobenzene	2 : 1	$C_{26}H_{18}O_{15}N_6$	Pale yellow needles	89°	N = 12.89	12.85
Quinol disalicylate and <i>s</i> -tri- nitrobenzene	2 : 1	$C_{32}H_{20}O_{18}N_6$	Yellow prisms	170°	N = 11.23	10.82
+Methyl salicylate and <i>s</i> -tri- nitrobenzene	2 : 1	$C_{20}H_{17}O_9N_3$	Pale yellow, crystalline mass	about 80°	—	—
Pyrogallol and <i>s</i> -trinitrobenzene	1 : 1	$C_{12}H_9O_9N_3$	Canary-yellow, prismatic needles	163°	N = 12.84	12.39
2 : 7-Dihydroxynaphthalene and <i>s</i> -trinitrobenzene	1 : 1	$C_{16}H_{11}O_8N_3$	{ Brown, transparent prisms (benzene) } { Flat, brown plates (glacial acetic acid) }	162°	N = 11.11	11.26
Potassium α -naphthoxide and <i>s</i> -trinitrobenzene	—	—	Dark green precipitate	decomposed	—	—
1-Bromo-2-naphthol and <i>s</i> -tri- nitrobenzene	1 : 1	$C_{16}H_{10}O_7N_3Br$	Canary-yellow needles	148°	Br = 18.1	18.3

Components.	Mols. of nitro- compound : mols. of phenol.	Formula.	Appearance.	M. p.	Analysis.	
					Found, per cent.	Calc., per cent.
2 : 4-Dibromo-1-naphthol and <i>s</i> -trinitrobenzene	1 : 1	$C_{16}H_9O_7N_3Br_2$	Yellow needles	97°	Br = 30.5	31.06
* <i>ar</i> -Tetrahydro- α -naphthol and <i>s</i> -trinitrobenzene	1 : 1	$C_{16}H_{15}O_7N_3$	Golden-yellow, prismatic needles	106—107°	N = 11.42	11.63
+ <i>iso</i> Eugenol and <i>s</i> -trinitrobenzene	1 : 1	$C_{16}H_{13}O_8N_3$	Bright crimson needles	70°	—	—
Hydroxyquinoline and <i>s</i> -trinitrobenzene	1 : 1	$C_{15}H_{10}O_7N_4$	Sulphur-yellow needles	123.5—124	N = 15.73	15.64
<i>m</i> -Hydroxyquinoline and <i>s</i> -trinitrobenzene	1 : 2	$C_{24}H_{17}O_8N_5$	Greenish-yellow, lance-shaped prisms	199—200° (decomp.)	N = 13.9	13.95
<i>p</i> -Hydroxyquinoline and <i>s</i> -trinitrobenzene	1 : 1	$C_{15}H_{10}O_7N_4$	Brownish-yellow plates	193—195°	N = 15.78	15.64
Hydroxylepidine and <i>s</i> -trinitrobenzene	1 : 2	$C_{26}H_{21}O_8N_5$	Canary-yellow prisms	227—228°	N = 13.21	13.18
Hydroxy-2-methylquinoline and <i>s</i> -trinitrobenzene	1 : 1	$C_{16}H_{12}O_7N_4$	Canary-yellow, felted needles	200—201°	N = 14.84	15.06
α -Naphthol and α -trinitro-naphthalene	1 : 1	$C_{20}H_{13}O_7N_3$	Brilliant red needles	117°	N = 10.54	10.32
* β -Naphthol and α -trinitro-naphthalene	1 : 1	$C_{20}H_{13}O_7N_3$	Orange-red needles	142°	N = 10.46	10.32
β -Naphthol and α -trinitro-naphthalene	2 : 1	$C_{30}H_{18}O_{13}N_6$	Bright red prisms	148°	N = 12.77	12.54
* α -Naphthol and β -tetranitro-naphthalene	1 : 1	$C_{20}H_{12}O_9N_4$	Scarlet needles	190—195° (decomp.)	N = 12.21	12.39
* β -Naphthol and β -tetranitro-naphthalene	1 : 1	$C_{20}H_{12}O_9N_4$	Orange-yellow needles	190—200° (decomp.)	N = 12.33	12.39
* β -Naphthol and <i>s</i> -trinitro-toluene	1 : 1	$C_{17}H_{13}O_7N_3$	Canary-yellow needles	110°	N = 11.33	11.32

II.—Additive Compounds of Phenolic Ethers with Aromatic Polynitro-derivatives.

Components.	Mols. of nitro- compound : mols. of phenol.	Formula.	Appearance.	M. p.	Analysis.	
					Found, per cent.	Calc., per cent.
*Quinol dimethyl ether and s-trinitrobenzene	2 : 1	$C_{20}H_{16}O_{14}N_6$	Long, bright red prisms	86.5°	N = 15.05	14.89
*Pyrogallol trimethyl ether and s-trinitrobenzene	1 : 1	$C_{15}H_{13}O_9N_3$	Flat, lustrous, bright yellow prisms	81°	N = 11.06	11.02
*Orcinol dimethyl ether and s-trinitrobenzene	1 : 1	$C_{15}H_{13}O_8N_3$	Orange-yellow needles	51—52°	N = 11.55	11.51
Piperonal and s-trinitrobenzene	1 : 1	$C_{14}H_9O_9N_3$	Golden-yellow plates	79°	N = 11.15	11.57
*Safrole and s-trinitrobenzene	1 : 1	$C_{16}H_{13}O_8N_3$	Golden-yellow plates	51°	{ t-nitro- benzene = 55.8	56.8
isoSafrole and s-trinitrobenzene	1 : 1	$C_{16}H_{13}O_8N_3$	Bright scarlet needles	85—86°		56.8
*Apiole and s-trinitrobenzene	1 : 1	$C_{18}H_{17}O_{10}N_3$	Orange-red plates	34—35°	{ trinitro- benzene = 54.4	9.65
isoApiole and s-trinitrobenzene	1 : 1	$C_{18}H_{17}O_{10}N_3$	Orange-red needles	67°		9.65
*isoEugenyl methyl ether and s-trinitrobenzene	1 : 1	$C_{17}H_{17}O_8N_3$	Bright scarlet plates	69—70°	—	—
Asarone and s-trinitrobenzene	2 : 1	$C_{34}H_{22}O_{15}N_6$	Deep prune needles (alcohol)	92.5°	N = 13.36	13.25
Asarone and s-trinitrobenzene	1 : 1	$C_{18}H_{19}O_9N_3$	Lighter prune, prismatic needles (benzene)	77—78°	N = 10.12	10.00
2 : 4 : 6 - Trimethoxyphenyl- 3 : 4-dimethoxystyryl ke- tone and s-trinitrobenzene	2 : 1	$C_{32}H_{26}O_{18}N_6$	Orange-red needles	106°	N = 10.87	10.71
α-Naphthyl methyl ether and s-trinitrobenzene	1 : 1	$C_{17}H_{13}O_7N_3$	Slender, canary-yellow needles	137—138°	N = 11.38	11.32
α-Naphthyl ethyl ether and s-trinitrobenzene	1 : 1	$C_{18}H_{15}O_7N_3$	Sulphur-yellow needles	125.5°	N = 10.92	10.90
α-Naphthyl phenyl ether and s-trinitrobenzene	1 : 1	$C_{22}H_{19}O_7N_3$	Dirty yellow plates	112.5°	N = 9.76	9.70

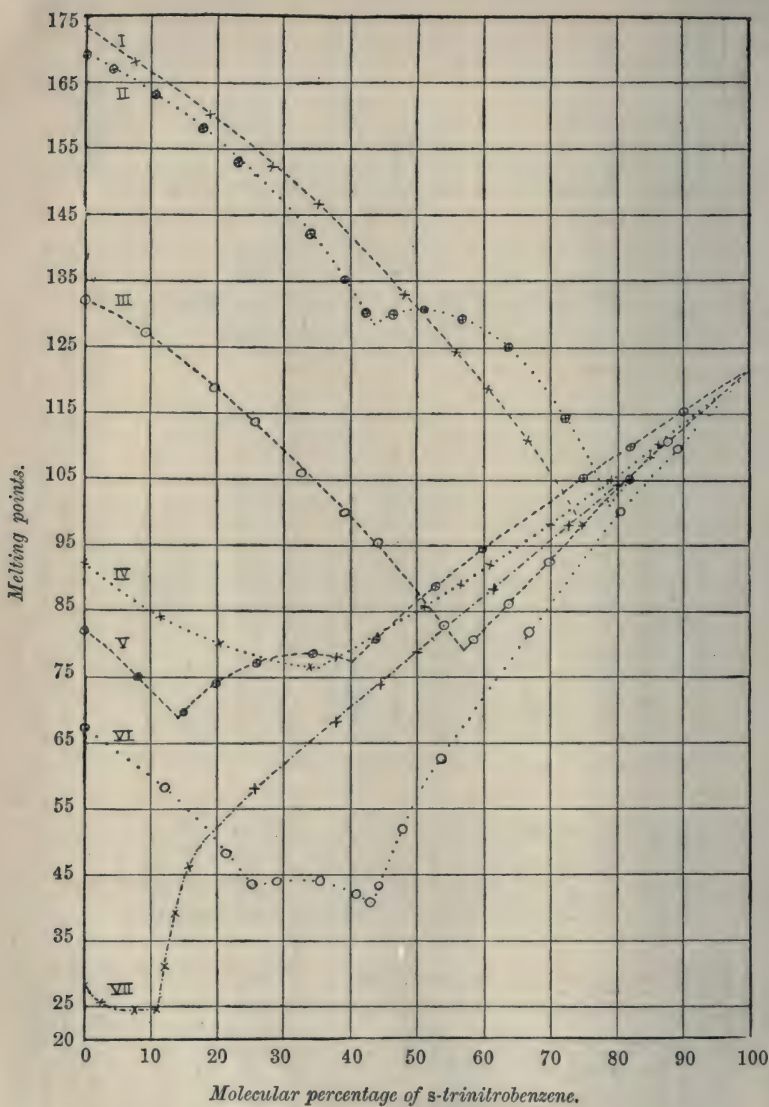
Components.	Mols. of nitro- compound : mols. of phenol.	Formula.	Appearance.	M. p.	Analysis.	
					Found, per cent.	Calc., per cent.
β -Naphthyl methyl ether and s-trinitrobenzene	1 : 1	$C_{17}H_{13}O_7N_3$	Long, canary-yellow needles	93.5°	N = 11.15	11.32
β -Naphthyl ethyl ether and s-trinitrobenzene	1 : 1	$C_{18}H_{15}O_7N_3$	Pale canary-yellow needles	95°	N = 10.90	10.90
β -Naphthyl phenyl ether and s-trinitrobenzene	2 : 1	$C_{26}H_{19}O_{13}N_5$	Bright lemon-yellow needles	105.5°	N = 12.95	13.00
β -Naphthyl ether and s-tri- nitrobenzene	2 : 1	$C_{32}H_{29}O_{13}N_5$	Yellow plates	128°	N = 11.8	12.07
2 : 7 - Dimethoxynaphthalene and s-trinitrobenzene	1 : 1	$C_{18}H_{15}O_8N_3$	Orange-yellow needles	111.5°	N = 10.57	10.47
β -Naphthyl ether and s-tri- nitrobenzene	1 : 1	$C_{27}H_{19}O_7N_3$	Light yellow, feathery needles	72°	N = 8.6	8.45
*Quinol dimethyl ether and s-trinitrobenzene	1 : 1	$C_{15}H_{15}O_8N_3$	Golden-brown, prismatic needles	45°	N = 11.74	11.51
*Pyrogallol trimethyl ether and s-trinitrobenzene	1 : 1	$C_{16}H_{17}O_9N_3$	Thick, dark yellow needles	56.5°	N = 10.57	10.63

III.—Additive Compounds of Cyclic Oxygen Compounds with Aromatic Polynitro-derivatives.

Coumarone and s-trinitro- benzene	1 : 1	$C_{14}H_9O_7N_3$	Long, flat, pale yellow plates	103.5—104°	$\left\{ \begin{array}{l} \text{trinitro-} \\ \text{benzene} \end{array} \right\}$ = 64.0		64.4
Diphenylene oxide and s-tri- nitrobenzene	1 : 1	$C_{18}H_{11}O_7N_3$	Lemon-yellow needles	96°	N = 11.12	11.02	11.02
α -Dinaphthylene oxide and s-trinitrobenzene	1 : 1	$C_{26}H_{19}O_7N_3$	Slender, brownish needles	183.5°	N = 8.8	8.73	8.73

* These compounds were prepared by using an excess of the phenol or phenolic ether. When the theoretical amounts of the components are used in the presence of alcohol or benzene as solvent, s-trinitrobenzene usually separates.

† These compounds were prepared by fusing the two components in the absence of a solvent, and are resolved into their components on the addition of a solvent.



Melting-point curves :

- | | |
|------|---|
| I. | <i>s</i> -Trinitrobenzene and xanthone. |
| II. | " " quinol. |
| III. | " " dimethylpyrone. |
| IV. | " " <i>s</i> -tribromophenol. |
| V. | " " fluorenone. |
| VI. | " " coumarin. |
| VII. | " " phenyl ether. |

been prepared, and it is noticeable that the colours of these compounds are much more pronounced than those of the additive compounds of the same phenols with trinitrobenzene.

s-Trinitrotoluene also forms compounds with phenols and their derivatives, but on the whole they are less stable than the products derived from trinitrobenzene.

In several instances, melting-point curves have been constructed in order to determine whether there is combination between trinitrobenzene and certain oxygen compounds. By this method we have been able to show that dimethylpyrone, xanthone, *s*-tribromophenol, and phenyl ether do not form additive compounds, and that coumarin yields an excessively unstable product; fluorenone and quinol more stable compounds.

IV.—*Melting-point Curves.*

The seven curves given in the diagram show that the cyclic oxygen compounds, coumarin and fluorenone (diphenylene oxide), yield additive compounds with *s*-trinitrobenzene in the absence of a solvent, whereas xanthone and dimethylpyrone do not. Quinol also forms an additive compound, which is comparatively stable, but diphenyl ether and *s*-tribromophenol do not.

V.—*Non-formation of Additive Compounds.*

The following compounds do not appear to yield additive compounds with trinitrobenzene in the presence of a solvent: *p*-Hydroxyacetophenone, 2:4-dihydroxybenzoic acid, and the isomeric 2:5-dihydroxy-acid, quinic acid and its ester, triphenylcarbinol, *p*-diphenol, diethylresorcinol, eugenol, eugenyl methyl ether, *p*-dihydroxydiphenylmethane, benzil, and benzoin.

In conclusion, we wish to thank Mr. F. Tutin for a specimen of 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone, and the Council of the Society for a grant which has covered part of the cost of this investigation.

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XXVI.—*The Relative Effect of Ethylenic and Acetylenic Linkings on Optical Rotatory Power.*

By THOMAS PERCY HILDITCH (1851 Exhibition Scholar).

THE study, by means of several series of esters and alkaloid salts, of the relative effects of ethylenic and acetylenic linkings on optical rotatory power has shown that Walden's simple rule that the rotatory power of the acetylenic member is intermediate between those of the saturated and ethenoid derivatives (*Zeitsch. physikal. Chem.*, 1896, **20**, 569) does not always hold good. Only two complete series of acids have, however, been used in this connexion— β -phenylpropionic, cinnamic, and phenylpropionic acids, and succinic, fumaric, maleic, and acetylenedicarboxylic acids. Further, in every instance so far observed, the ethylenic ester or salt shows an increase in rotatory power over the corresponding saturated compound, variations having appeared only in the relative effect of the acetylenic derivative. It is nevertheless probable that this consistent increase is due rather to the reinforcing effect of the contiguous carboxyl group than to the simple ethenoid radicle, for optically active compounds containing this grouping unconjugated with other unsaturated residues possess sometimes an enhanced and sometimes a diminished rotatory power:

	[M] _D	Difference.
Menthyl <i>n</i> -propyl ether (Tschugaeff, <i>J. Russ. Phys. Chem. Soc.</i> , 1902, 34 , 606)	-182.5	—
Menthyl allyl ether (Haller and March, <i>Compt. rend.</i> , 1904, 136 , 1635)	193.1	+10.6
<i>n</i> -Propyl santonate (Carnelutti and Nasini, <i>Ber.</i> , 1880, 13 , 2208)	+120.4	—
Allyl santonate (Carnelutti and Nasini, <i>Ber.</i> , 1880, 13 , 2208)	120.2	-0.2
Tartarodi- <i>n</i> -propylamide (Frankland and Twiss, <i>Trans.</i> , 1906, 89 , 1852)	+290.0	—
Tartarodiallylamide (Frankland and Twiss, <i>Trans.</i> , 1906, 89 , 1852)	273.0	-15.0

No similar active compound containing a simple acetylenic residue has apparently yet been prepared, but even when reinforced by the presence of an adjacent carboxyl group the effect of this linking is curiously uncertain. In two cases, indeed, the relative effects of the ethenoid and acetylenic groups appear to be determined by the solvent in which the polarimetric readings are made. For example, the author found that menthyl phenylpropiolate showed less rotatory power than either menthyl cinnamate or menthyl β -phenylpropionate in chloroform or acetone solutions (*Trans*, 1908, **93**, 1), whilst Rupe (*Annalen*, 1909, **369**, 311) states that in benzene these esters conform to Walden's rule. Since the specimens used in the former

experiments furnished, when dissolved in benzene, numbers agreeing with those of Rupe, the discrepancy cannot be due to impurity or other experimental error in either case. The second example of this kind has occurred in the course of the work now being described.

The order of effect of unsaturation for amyl esters and coniine salts of the cinnamic series of acids is the same, but differs from that of salts of the more complicated alkaloids, brucine, codeine, or cinchonine (Trans., 1908, **93**, 700). It was thought that this might indicate that the rule was true for compounds of a simple optically active structure, and therefore the same esters of *d*-methylhexylcarbinol (*d*-*sec*-octyl alcohol) were prepared, and, in view of the experience with the menthyl esters, were examined in chloroform and benzene, as well as in the liquid condition. Two distinct series of specimens (from different samples of active octyl alcohol) showed practically the same activity. The order observed was, however, not that anticipated, for, although the esters themselves just succeeded in conforming to the rule, the acetylenic compound possessed the greatest anomaly of the three in chloroform or benzene solution.* The anomaly in rotatory power has been based, as usual, on the differences, " $[D]_D$," from the mean molecular rotation of the higher fatty acid esters, and the data used in determining the latter "normal value" were as follows:

(a) *Without Solvent.*

	$d\ 20^\circ/4^\circ$.	$[\alpha]_D$.	$[M]_D$.
<i>d</i> -Methylhexylcarbinol	0.8216	+9.57	+12.4
<i>d</i> -Methylhexylcarbiny <i>n</i> -butyrate ...	0.8633	+8.20	+16.4
" <i>n</i> -pentoate ..	0.8580	8.58	18.3
" <i>n</i> -hexoate	0.8562	8.43	19.2
Mean molecular rotation	—	—	+18.0

(b) *In Solution (2.5 per cent.).*

	Chloroform.		Benzene.	
	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.
<i>d</i> -Methylhexylcarbinol	+8.76	+11.4	—	—
<i>d</i> -Methylhexylcarbiny <i>n</i> -butyrate	+4.00	+8.00	+1.04	+2.08
" <i>n</i> -pentoate	3.72	7.96	0.96	2.05
" <i>n</i> -hexoate	3.52	8.03	0.92	2.10
Mean molecular rotation.....	—	+8.0	—	+2.1

The values observed in the esters studied are collected in the next table.

* It must be remarked that in all three cases the difference in $[M]_D$ between *d*-*sec*-octyl cinnamate and phenylpropiolate is less than 1.5 per cent.

(a) *Without Solvent* (length of tube 0.1-dcm.; temperature 22°).

	<i>d</i> 20°/4°.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
<i>d</i> -Methylhexylcarbinyll β -phenylpropionate	0.9426	+11.92	+31.2	+13.2
„ cinnamate	0.9645	35.32	91.8	73.8
„ phenylpropionate	0.9876	35.08	90.5	72.5

(b) *In Solution* (2.5 per cent.; length of tube 1.0-dcm.; temperature 22°).

	Chloroform.			Benzene.		
	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
<i>d</i> -Methylhexylcarbinyll β -phenylpropionate.	+11.52	+30.2	+22.2	+6.00	+15.7	+13.6
<i>d</i> -Methylhexylcarbinyll cinnamate	30.40	79.1	71.1	33.04	85.9	83.8
<i>d</i> -Methylhexylcarbinyll phenylpropionate ...	30.88	79.7	71.7	35.12	90.6	88.5

The data derived from the succinic acid series has been based up to the present only on their alkaloidal salts, but the respective mono- and di-menthyl esters have now been prepared, and this survey of the relative effects of ethylenic and acetylenic groups on rotatory power will be concluded by quoting the figures so obtained. The measurements were made in chloroform and acetone solutions at concentrations of about 5 and 2.5 per cent. Since concentration has little effect on the optical activity in these examples, it will suffice to give the results for one dilution only in each case; the temperature of measurement varied between 22° and 23.5°.

Menthyl Hydrogen Esters: 2.0 per cent. solutions.

	In chloroform.			In acetone.		
	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
Succinate	-66.00	-169.0	+7.8	-65.50	-167.7	+6.5
Fumarate	71.25	180.9	19.7	69.25	175.9	14.7
Acetylenedicarboxylate ...	67.75	170.6	9.4	68.75	173.3	12.1

Dimenthyl Esters: 2.5 per cent. solutions.

	In chloroform.			In acetone.		
	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
Succinate	-82.4	-324.6	+1.1	-81.4	-320.7	-0.8
Fumarate	100.6	394.3	36.0	99.4	389.6	+33.6
Acetylenedicarboxylate	84.2	328.4	3.0	85.6	333.9	5.8

The whole of the results now available may conveniently be summarised at this point:

Acid series.	Optically active system.	Solvent.	Rotatory power of :		
			Saturated.	Ethylenic.	Acetylenic.
Cinnamic, etc.	Amyl esters. *	—	Least.	Greatest.	Inter-mediate.
"	sec.-Octyl esters.	—	"	"	"
"	Menthyl esters. †	Benzene.	"	"	"
Succinic, etc.	Menthyl acid esters.	{ Chloroform }	"	"	"
"	Dimenthyl esters.	{ or acetone. }	"	"	"
Cinnamic, etc.	Coniine salts.	Chloroform.	"	"	"
"	sec.-Octyl esters.	{ Chloroform }	"	Inter-mediate.	Greatest.
"		{ or benzene. }	"	"	"
"	Brucine salts.	Chloroform.	"	"	"
"	Cinchonine salts.	"	"	"	"
"	Codeine.	"	"	"	"
Succinic, etc.	Coniine.	"	"	"	"
"	Cinchonine.	"	"	"	"
"	Codeine.	"	"	"	"
Cinnamic, etc.	Menthyl esters.	{ Chloroform }	Inter-mediate.	Greatest.	Least.
"	Bornyl esters.	{ or acetone. }	"	"	"
Succinic, etc.	Brucine salts.	Chloroform.	"	Least.	Greatest.

* Walden, *loc. cit.*† Rupe, *loc. cit.*

The most interesting points appear to be :

(a) There is no general rule to cover the relative effect of trebly- and doubly-linked carbon atoms.

(b) It is curious that in about half of the series examined the optical activity of the acetylenic compound approximates very nearly to that of either the saturated or the ethenoid derivative. This must, however, be attributed to coincidence, since it is sometimes the ethenoid and sometimes the saturated compound to which close resemblance is found.

(c) It would appear that, in addition to unsaturation, other factors must contribute powerfully to the total determinant of the rotatory power, and that whilst the influence of an ethenoid bond seems to be sufficiently strong to cause a uniform optical effect throughout, that of the acetylenic linking is less definite, and therefore more liable to be perturbed or masked by those due to other factors.

(d) The menthyl esters of the cinnamic, etc., series manifest a different order in benzene solution to that in chloroform or acetone, and the sec.-octyl esters of the same acids give a different order when examined without solvent to that displayed when in chloroform or benzene solution.

(e) Derivatives of cinnamic and phenylpropionic acids show greater and better-defined anomalies than those of any of the other acids; in view of investigations on the effect of contiguous unsaturated groups on optical activity, this may safely be ascribed to the enhancing influence of the benzenoid residue in conjugation with the double or triple carbon linking.

EXPERIMENTAL.

The active *d*-methylhexylcarbinol used was prepared from Kahlbaum's *sec*-octyl alcohol (compare Pickard and Kenyon, *Trans.*, 1907, **91**, 2058). The sample finally used boiled at 86—87°/20 mm., and had D_4^{20} 0.8216. The esters were made by heating equivalent quantities of the alcohol with the appropriate acid chloride at 100° for two or three hours, and, after other purification, were twice fractionated under diminished pressure before polarimetric examination; at Professor Guye's suggestion, the aliphatic compounds were analysed refractometrically as well as in the usual way (compare Guye and Jordan, *Bull. Soc. chim.*, 1896, [iii], **15**, 474). All the esters were colourless, agreeably-smelling oils.

d-Methylhexylcarbinyl *n*-butyrate boiled at 112°/20 mm., D_4^{20} 0.8633, n_D^{20} 1.41957, whence MR_D (found) = 58.57 (theory, 58.84):

0.1027 gave 0.2711 CO_2 and 0.1129 H_2O . $C = 71.99$; $H = 12.22$.

$C_{12}H_{24}O_2$ requires $C = 72.00$; $H = 12.00$ per cent.

d-Methylhexylcarbinyl *n*-pentoate boiled at 116—117°/20 mm., D_4^{20} 0.8580, n_D^{20} 1.42287, whence MR_D (found) = 63.50 (theory, 63.41):

0.1153 gave 0.3066 CO_2 and 0.1300 H_2O . $C = 72.51$; $H = 12.53$.

$C_{13}H_{26}O_2$ requires $C = 72.90$; $H = 12.15$ per cent.

d-Methylhexylcarbinyl *n*-hexoate boiled at 120—123°/20 mm., D_4^{20} 0.8562, n_D^{20} 1.42547, whence MR_D (found) = 68.30 (theory, 7.98):

0.0989 gave 0.2667 CO_2 and 0.1104 H_2O . $C = 73.53$; $H = 12.40$.

$C_{14}H_{28}O_2$ requires $C = 73.69$; $H = 12.28$ per cent.

d-Methylhexylcarbinyl β -phenylpropionate boiled at 196—197°/20 mm., D_4^{20} 0.9426, n_D^{20} 1.47762, whence $MR_D = 78.66$:

0.1238 gave 0.3518 CO_2 and 0.1066 H_2O . $C = 77.50$; $H = 9.57$.

$C_{17}H_{26}O_2$ requires $C = 77.85$; $H = 9.92$ per cent.

d-Methylhexylcarbinyl cinnamate boiled at 200°/25 mm., D_4^{20} 0.9645, n_D^{20} 1.51451, whence $MR_D = 81.22$:

0.1203 gave 0.3444 CO_2 and 0.1020 H_2O . $C = 78.09$; $H = 9.42$.

$C_{17}H_{24}O_2$ requires $C = 78.45$; $H = 9.23$ per cent.

d-Methylhexylcarbinyl phenylpropiolate boiled at 200—202°/25 mm., D_4^{20} 0.9876, n_D^{20} 1.51014, whence $MR_D = 78.15$:

0.1042 gave 0.3001 CO_2 and 0.0821 H_2O . $C = 78.56$; $H = 8.76$.

$C_{17}H_{22}O_2$ requires $C = 79.07$; $H = 8.53$ per cent.

The menthyl esters of the succinic acid series were prepared by heating about 5 grams of the acid with 8 grams of menthol to a temperature of 120—130° in sealed tubes for ten hours. The ethereal solution of the reaction product was filtered and extracted twice or three times with sodium carbonate solution. The ethereal layer was dried and evaporated, and the residue quickly distilled

in a current of steam to remove any excess of the alcohol. The residue furnished the *dimenthyl* ester on re-extraction with ether.

The alkaline extract, containing the salts from unchanged acid and acid ester, was treated with dilute sulphuric acid, and extracted with ether, whereby the *hydrogen* ester was obtained. In this way fairly good yields of the succinates were obtained, but the results with the other two acids were not so good. Great difficulty was found in obtaining the latter esters in the solid state; indeed, this was not attained in the case of menthyl hydrogen fumarate and dimenthyl acetylenedicarboxylate. Since the esters could not be distilled in a vacuum without decomposition, recourse was had to the method of purification used in the case of the liquid alkyl hydrogen camphorates (Edminson and Hilditch, Trans., 1909, 97, 225), after which the analytical numbers obtained agreed closely with those demanded by theory.

Menthyl hydrogen fumarate, $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, is a colourless, viscous oil, not crystallising when cooled in a mixture of solid carbon dioxide and acetone, decomposing and charring at about 200° :

0.1826 gave 0.4400 CO_2 and 0.1514 H_2O . $\text{C}=65.72$; $\text{H}=9.21$.

$\text{C}_{14}\text{H}_{22}\text{O}_4$ requires $\text{C}=66.14$; $\text{H}=8.66$ per cent.

Dimenthyl fumarate, $\text{C}_{10}\text{H}_{19}\cdot\text{CO}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, crystallised in very large, colourless prisms, and was only obtained solid with great difficulty in the first instance, thereafter crystallising readily from light petroleum, and melting at 55° :

0.1938 gave 0.5200 CO_2 and 0.1810 H_2O . $\text{C}=73.16$; $\text{H}=10.38$.

$\text{C}_{24}\text{H}_{40}\text{O}_4$ requires $\text{C}=73.47$; $\text{H}=10.21$ per cent.

Menthyl hydrogen acetylenedicarboxylate, $\text{CO}_2\text{H}\cdot\text{C}:\text{C}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, crystallises in small, wax-like needles, melting at 79° :

0.1096 gave 0.2690 CO_2 and 0.0780 H_2O . $\text{C}=66.92$; $\text{H}=7.91$.

$\text{C}_{14}\text{H}_{20}\text{O}_4$ requires $\text{C}=66.67$; $\text{H}=7.94$ per cent.

Dimenthyl acetylenedicarboxylate, $\text{C}_{10}\text{H}_{19}\cdot\text{CO}_2\cdot\text{C}:\text{C}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, is a colourless oil, not crystallising at the temperature of an acetone solution of solid carbon dioxide, and decomposing before boiling under diminished pressure (20 mm.):

0.1557 gave 0.4186 CO_2 and 0.0139 H_2O . $\text{C}=73.31$; $\text{H}=9.92$.

$\text{C}_{24}\text{H}_{38}\text{O}_4$ requires $\text{C}=73.84$; $\text{H}=9.74$ per cent.

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XXVII.—*The Effect of Contiguous Unsaturated Groups on Optical Rotatory Power. Part VI. The Influence of the Carbonyl Group on Optical Rotatory Power. Part VII. The Relative Influences of Aromatic and Hydroaromatic Nuclei on Optical Rotatory Power. Part VIII. The Influence on Optical Activity of Two Contiguous Unsaturated Groups in Comparison with that of One Unsaturated Group at Varying Distances from the Optically Active Complex.*

By THOMAS PERCY HILDITCH (1851 Exhibition Scholar).

PART VI.—*The Influence of the Carbonyl Group on Optical Rotatory Power.*

THE work of Walden (*Zeitsch. physikal. Chem.*, 1896, **20**, 569), Rupe (*Annalen*, 1903, **327**, 157), Hartwall (*Diss.*, Helsingfors, 1904), and the author (*Trans.*, 1908, **93**, 1, 700) has demonstrated that in general optically active esters and salts of acids containing an ethenoid group adjacent to the carboxyl group possess a greater degree of rotatory power than similar derivatives of the corresponding saturated acids. The present communication deals with an analogous series of compounds derived from ketonic acids, thus containing carbonyl in place of an ethenoid group in the above series.

The compounds chosen for the purposes of this investigation were the following:

Menthyl esters and brucine salts of glyoxylic, pyruvic, acetoacetic, and lævulic acids.

Brucine salts of mesoxalic, oxalacetic, and acetonedicarboxylic acids.

Brucine salts of certain aromatic ketonic acids.

The measurements of rotatory power were carried out in dry chloroform solution and in general at two dilutions, 5 grams per 100 c.c. and 2.5 grams per 100 c.c. of solution respectively. The length of solution used was 2-dm., and the temperature was maintained throughout at 20°. In the succeeding tables of results, there is given, in addition to the usual specific and molecular rotatory power, the "anomaly" $[D]_D$ based on the difference between the molecular rotatory power of the compound in question and the

"normal value," that is, the mean molecular rotatory power of the esters or salts of the higher normal fatty acids with menthol or brucine, as the case may be (compare *Trans.*, 1909, **95**, 1571).

I.—*Menthyl Esters of the Pyruvic Acid Series.*

	C : 5.			C : 2.5.		
	[α] _D .	[M] _D .	[D] _D .	[α] _D .	[M] _D .	[D] _D .
Menthyl pyruvate	-83.40	-188.5	+28.0	-82.00	-185.3	+24.1
„ acetoacetate { at once	—	—	—	68.36	164.1	2.9
„ { after 15 hours.	—	—	—	67.04	160.9	-0.3
„ lævulate	67.62	171.8	11.3	67.60	171.7	+10.5

Menthyl pyruvate and lævulinate showed no appreciable mutation.

II.—*Brucine Salts of the Pyruvic Acid Series.*

	C : 5.			C : 2.5.		
	[α] _D .	[M] _D .	[D] _D .	[α] _D .	[M] _D .	[D] _D .
Brucine glyoxylate	-12.50	-60.7	+186.7	-12.62	-61.3	+190.7
„ pyruvate	17.68	85.2	162.2	17.88	86.2	165.8
„ acetoacetate	11.02	54.7	192.7	10.82	53.7	198.3
„ lævulate	34.40	175.5	71.9	34.88	177.9	74.1

III.—*Dibrucine Salts of the Mesoxalic Acid Series.*

Dibrucine mesoxalate ...	-20.46	-189.1	+152.9	-20.70	-191.9	+156.1
„ oxalacetate ...	39.40	362.4	66.2	38.80	357.0	73.5
„ acetonedicarboxylate	45.84	428.2	33.3	45.84	428.2	37.9

IV.—*Brucine Salts of Aromatic Ketonic Acids.*

Brucine benzoate	-25.40	-131.1	+116.3	-25.00	-129.0	+123.0
„ phenylglyoxylate	6.00	32.6	214.8	6.14	33.4	218.6
„ phenylpyruvate.	+3.66	+20.4	267.8	+3.32	+18.5	270.5
„ benzoylacetate...	-32.26	-180.0	67.4	-33.83	-188.8	63.2
„ benzylpyruvate..	9.59*	54.9*	192.5	9.61*	55.5*	196.5
„ β -benzoyl propionate	32.18	184.1	63.3	31.88	182.4	69.6
„ benzoylpyruvate	+10.26	+60.1	307.5	+11.28	+66.1	318.1

* C : 4.32 and 2.16 respectively.

It will be seen that this system—carbonyl-carboxyl—follows in its main outlines the same rule as the other conjugated structures examined, the anomalies, prominent in those members containing the unsaturated residues adjacent to each other, rapidly declining as the latter are separated. One or two points, however, require special remark:

(a) One cannot always be certain that the carbonyl group is always present as such, since there frequently exists the possibility of an enolic structure in this part of the molecule.

(b) The carbonyl groups in glyoxylic and mesoxalic acids are modified by the addition of a molecule of water, thus lessening the total amount of residual affinity and to a certain extent invalidating the comparison. Consequently, if it be granted from the other examples that the carbonyl-carboxyl grouping enhances optical activity, the true anomalies in these two cases would be somewhat higher.

The series of aromatic ketonic acid salts is especially instructive, for in addition to confirming the general results arrived at from the aliphatic keto-acids, it further demonstrates that:

(a) The carbonyl group alone, when adjacent to the carboxyl group, creates an effect almost as pronounced as that of the benzoyl radicle (phenylpyruvic, benzylpyruvic acids).

(b) The benzoyl system, when separated by methylene groups from the asymmetric part of the molecule, ceases to a great extent to influence the activity (benzoylacetic and β -benzoylpropionic acids).

(c) The benzoyl system, accompanied in the same molecule by a conjugate carbonyl-carboxyl group, produces the maximum effect.

It therefore appears that the carbonyl group, like various other unsaturated groups, causes anomalies in molecular rotatory power; quantitatively speaking, the polarimetric effect of the carbonyl group is probably somewhat less than that of an ethenoid residue under similar conditions. On the other hand, adjacent carbonyl and carboxyl groups together exert an influence on optical activity comparable to that displayed by a benzoyl radicle—a system possessed of considerable residual affinity.

Finally, either by separating the adjacent unsaturated groups or by removing the conjugated system en bloc away from the optically active complex, the anomaly in optical rotatory power may be much diminished or even caused to disappear.

PART VII.—*The Relative Influences of Aromatic and Hydroaromatic Nuclei on Optical Rotatory Power.*

Although no fresh physical evidence as to the absolute structural condition of the "benzene ring" is yet available from the rotatory power of optically active aromatic compounds, one may conclude from the values given by Rupe and his students (*loc. cit.*) for certain menthyl esters of hydroaromatic acids that the successive

introduction of ethylene bonds, culminating finally in an aromatic nucleus, progressively increases optical activity:

	[M] _D .	[D] _D .
Menthyl <i>cyclohexanecarboxylate</i>	- 157.2	- 3.3
„ Δ^1 - <i>cyclohexanecarboxylate</i>	197.0	+ 36.5
„ benzoate.....	217.2	56.7
„ Δ^1 - <i>ac-tetrahydro-α-naphthoate</i> ...	- 215.6	+ 55.1
„ α - <i>naphthoate</i>	245.3	84.8

There is, however, nothing to show whether the maximum influence of the phenyl group is due to three conjugated ethylenic bonds or to the residual affinity of the radicle as a whole, and accordingly for the purpose of the present paper the benzenoid residue is regarded as a single unsaturated group.

Some experiments, which incidentally illustrate the conditions under which ring-formation affects optical activity, have been carried out by the author to determine the nature of the influence of the aromatic residue from the rotatory powers of salts of various corresponding aromatic and hydroaromatic bases with some optically active acids.

The solutions designed for measurement in the polariscope were made up from the accurately weighed requisite amounts of the base and acid concerned, and the salts formed were subsequently recovered for analysis, etc.

The acids chosen were *d*-camphoric, *d*-camphor- π -sulphonic, and *d*-tartaric; the use of chloroform as a solvent, which is particularly desirable in the case of salts owing to its non-hydroxylic nature, was precluded in the salts of camphoric and tartaric acids by reason of insolubility. Consequently it was necessary to use alcohol for the camphorates, and water for the tartrates. The presence of an ionising solvent introduces a conflicting influence—the constant “molecular” rotation of ions (Oudemans-Landolt law); nevertheless, probably in consequence of incomplete dissociation, differences were found of the same qualitative nature as those manifested in the case of the camphor- π -sulphonates.

In order to obtain a basis for the approximate numerical estimation of anomalies, it was desirable to ascertain the molecular rotatory power of salts of these acids with the normal aliphatic amines.

Since the volatility of the lowest members of the fatty amines rendered them difficult to manipulate in these experiments, whilst the higher members are difficult to obtain, the molecular rotatory power of the *n*-butylamine salts of the acids employed was accepted as an approximate series constant (Tschugaeff, *Ber.*, 1898, **31**, 360,

1775; Hilditch, Trans., 1909, **95**, 1571), and the following values were thus obtained:

	Solvent.	C : 5 per cent.		C : 5 per cent.	
		$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.
Camphoric acid.....	Alcohol	+48.02	+96.0	+47.72	+95.4
Di- <i>n</i> -butylamine camphorate...	,,	+10.96	+37.9	+11.16	+38.6
Camphor- π -sulphonic acid.....	Chloroform	+24.82	+57.6	+24.04	+55.8
<i>n</i> -Butylamine camphor- π -sulphonate	,,	+20.36	+62.1	+20.44	+62.3
Tartaric acid.....	Water	+14.02	+21.0	+14.44	+21.7
Di- <i>n</i> -butylamine tartrate	,,	+17.86	+52.9	+17.40	+51.5

The following tables show the polarimetric results derived from the various salts studied:

I.—Neutral Camphorates in Alcohol.

Base.	C : 5 per cent.			C : 2.5 per cent.		
	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
Aniline	+32.50	+125.4	+87.5	+31.84	+122.9	+84.3
Pyridine	25.90	92.7	54.8	27.12	97.1	58.5
Piperidine	14.24	52.7	14.8	14.36	53.1	14.5
Quinoline	+19.16	+87.7	+49.8	+18.76	+85.9	+47.3
Tetrahydroquinoline	17.56	81.8	44.9	17.28	80.5	41.9
α -Naphthylamine	+18.12	+88.1	+50.2	+18.00	+87.5	+48.9
<i>ar</i> -Tetrahydro- α -naphthylamine	16.92	83.6	45.7	16.76	82.8	44.2
β -Naphthylamine	+18.64	+90.6	+52.7	+18.72	+91.0	+52.4
<i>ac</i> -Tetrahydro- β -naphthylamine	14.38	71.0	33.1	14.32	70.7	32.1

II.—Camphor- π -sulphonates in Chloroform.

Base.	C : 5 per cent.			C : 2.5 per cent.		
	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
Aniline	+23.28	+75.7	+13.6	+23.32	+75.8	+13.5
Pyridine	31.42	97.7	35.6	31.72	98.7	36.4
Piperidine	22.94	72.7	10.6	21.40	67.8	5.5
Quinoline	+27.90	+100.7	+38.6	+26.96	+97.3	+35.0
Tetrahydroquinoline	25.98	94.8	32.7	25.36	92.6	30.3
α -Naphthylamine	+21.38	+80.2	+18.1	+20.92	+78.4	+16.1
<i>ar</i> -Tetrahydro- α -naphthylamine	19.92	75.5	13.4	19.80	75.0	12.7
β -Naphthylamine	+21.54	+80.8	+18.7	+20.80	+78.0	+15.7
<i>ac</i> -Tetrahydro- β -naphthylamine	17.36	65.8	3.7	17.36	65.8	3.5

III.—*Neutral Tartrates in Water.*

Base.	C : 5 per cent.			C : 2·5 per cent.		
	[α] _D .	[M] _D .	[D] _D .	[α] _D .	[M] _D .	[D] _D .
Aniline	+16·58	+55·7	+2·8	+16·12	+54·2	+2·7
Pyridine	19·30	59·5	6·6	18·72	57·7	6·2
Piperidine	17·12	54·8	1·9	16·80	53·8	2·3
Quinoline	+13·22	+54·0	+1·2	+12·80	+52·2	+0·7
Tetrahydroquinoline	13·42	55·8	2·9	12·80	53·3	1·8

The anomalies in the diquinoline tartrate group are not outside the limits of experimental error, and it was impossible to employ the naphthylamine tartrates on account of their sparing solubility.

Analysing these results (which, it must be conceded, are, for optical activity, remarkably consistent), we have:

Base.	Constitution.	Anomaly shown in rotatory power.
(a) Aniline.	Benzenoid conjugated with amino-group.	Well defined.
Pyridine.	Benzenoid group.	Well defined.
Piperidine.	Alicyclic group.	Relatively small.
(b) Quinoline.	Two conjugated aromatic nuclei.	Well defined.
Tetrahydroquinoline.	Aromatic system + alicyclic amine, the former being also adjacent to the secondary amino-group.	Almost as pronounced as that due to quinoline.
(c) α -Naphthylamine.	Amino-group adjacent to two conjugated aromatic nuclei.	Well defined.
<i>ar</i> -Tetrahydro- α -naphthylamine.	Alicyclic + benzenoid systems, the latter still contiguous to the amino-group.	Slightly less than with α -naphthylamine.
(d) β -Naphthylamine.	Similar to α -naphthylamine.	Much the same as α -naphthylamine.
<i>ac</i> -Tetrahydro- β -naphthylamine.	Alicyclic + benzenoid systems, the latter separated by the former from the amino-group.	Relatively small.

The whole series therefore shows very clearly the enhancing effect of an aromatic group as contrasted with the very small effect of a hydroaromatic nucleus. The only other instance of reduced naphthylamine derivatives (which are obviously exceptionally suited for this comparison) is exactly parallel (Frankland and Ormerod, *Trans.*, 1903, **83**, 1342):

	[M] _D .
Tartarodi- β -naphthylamide	+1163
Tartarodi- <i>ar</i> -tetrahydro- β -naphthylamide	840
Tartarodi- <i>ac</i> -tetrahydro- β -naphthylamide	240

These results show that a benzenoid group, when united to another unsaturated group, enhances optical activity, and that the preponderating factor is its unsaturated nature, its ring-structure having very little to do with its influence on rotatory power.

It is frequently stated that ring-formation usually profoundly alters the rotation of a substance, but a brief examination of the literature will reveal that, while this is very true when the asymmetric atoms themselves take part in the formation of the ring system, in all other cases corresponding open- and closed-chain compounds show only small and indefinite changes.

By way of example, and in addition to the results above, we may quote those of Rupe (*loc. cit.*):

	[M] _{D.}	[M] _{D.}	
Menthyl cyclopropanecarboxylate.....	-153.5	-164.7	Menthyl <i>n</i> -butyrate.
„ cyclobutanecarboxylate	164.4	165.7	„ <i>n</i> -valerate.
„ cyclopentanecarboxylate.....	171.3	164.7	„ <i>n</i> -hexoate.
„ cyclohexanecarboxylate	157.2	165.9	„ <i>n</i> -heptoate.

PART VIII.—*The Influence on Optical Activity of Two Contiguous Unsaturated Groups in Comparison with that of One Unsaturated Group at Varying Distances from the Optically Active Complex.*

Attention was drawn by Tschugaëff (*loc. cit.*) to the rotatory power of the first three members of menthyl esters of the homologous phenyl aliphatic acids and to those of the corresponding amyl esters (Guye and Chavanne, *Bull. Soc. chim.*, 1896, [iii], **15**, 177), pointing out that the value in both, abnormally large in the benzoates, decreased to almost the average value of esters of a normal aliphatic acid when the third member was reached:

Ester.	Amyl.		Menthyl.	
	[M] _{D.}	[D] _{D.}	[M] _{D.}	[D] _{D.}
Mean value of fatty acid ester	+4.33	—	-157.8	—
Benzoate	+9.52	+5.19	-236.3	+78.5
Phenylacetate	7.91	3.58	190.7	32.9
β-Phenylpropionate	4.73	0.40	161.9	4.1

The brucine and cinchonine salts of the same acids, more recently examined by the author (*Trans.*, 1908, **93**, 1388), show the same gradation in optical anomaly.

Tschugaëff concluded that the power of an unsaturated group to affect optical activity rapidly declined as it was separated from the asymmetric system, and Guye (*Proc.*, 1901, **17**, 48) adopted these examples as particular cases of his more general conclusion that substitution at a point sufficiently removed from the asymmetric atom creates little optical effect.

Rupe (*loc. cit.*) elaborated the question by his work on isomeric pentenoic and hexenoic menthyl esters, and suggested that the size

of the anomaly produced by unsaturation is determined mainly by the proximity of the unsaturated group to the asymmetric system :

	[M] _D .
Menthyl $\Delta^{\alpha\beta}$ -pentoate	- 177.1
„ $\Delta^{\beta\gamma}$ -pentoate	172.5
„ $\Delta^{\gamma\delta}$ -pentoate	160.2
„ $\Delta^{\alpha\beta}$ -hexenoate	- 172.4
„ $\Delta^{\beta\gamma}$ -hexenoate	164.1
„ $\Delta^{\gamma\delta}$ -hexenoate	153.5
„ $\Delta^{\delta\epsilon}$ -hexenoate	154.4

The author has in previous papers (Trans., 1909, **95**, 336, 1570, etc.) attributed many cases of abnormal rotatory power to the presence of adjacent or "conjugated" unsaturated systems in the molecules in question, and it appears well to discuss in detail those cases which are at first sight equally well covered either by the latter or by the Tschugaeff-Rupe explanation. For it must be observed that in the examples from which these authors' deductions are made, a carboxyl residue always intervenes between the phenyl and asymmetric radicles, and thus, simultaneously with increasing distance of the phenyl group from the asymmetric system, the contiguity of the unsaturated phenyl and carboxyl residues is automatically destroyed.

It is interesting in this connexion to notice that in the case of some neutral aniline and benzylamine salts of optically active acids, in which the benzenoid and carboxyl residues are separated by a (saturated) quinquivalent nitrogen atom, the decrease in optical activity is not always so marked as in the former instances of simple aromatic esters and salts. These examples, which were observed under the same conditions as the similar salts described on a preceding page, are collected in the next table.

Acid.	Solvent.	Percentage concentration.	Aniline salt.			Benzylamine salt.		
			[α] _D .	[M] _D .	[D] _D .	[α] _D .	[M] _D .	[D] _D .
Camphoric	Alcohol	5.0	+ 32.50	+ 125.4	+ 87.5	+ 16.92	+ 70.0	+ 32.1
„	„	2.5	31.84	122.9	84.3	17.16	71.0	32.4
Camphor- π -sulphonic	Chloroform	5.0	+ 23.28	+ 75.7	+ 13.6	+ 22.00	+ 74.6	+ 12.5
Camphor- π -sulphonic	„	2.5	23.32	75.8	13.5	21.36	72.4	10.1
Tartaric	Water	5.0	+ 16.58	+ 55.7	+ 2.8	+ 18.28	+ 66.5	+ 13.7
„	„	2.5	16.12	54.2	2.7	17.40	63.3	11.8

If, on the other hand, compounds are selected in which it is possible, while maintaining the same relative positions of unsaturated groups to asymmetric system, to alter the amount of residual affinity (and therefore of any effect due to conjugation) by changing the character of one of the unsaturated radicles, the results obtained are very different. In some cases, for example,

one can compare corresponding benzyl and benzoyl derivatives of an active substance, when, whilst the phenyl group is left at the same distance from the active complex, there is in one case a single phenyl group and in the other a conjugated (phenyl+carbonyl) system.

We may thus compare some ethers of menthol described by Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606) with the esters to which reference has already been made:

	[M] _D	Difference.
Menthyl ethyl ether, $\text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_{19}$	-179.0	53.7
Menthyl benzyl ether, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_{19}$	-232.7	
Menthyl acetate, $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{10}\text{H}_{19}$	-157.3	79.0
Menthyl benzoate, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{10}\text{H}_{19}$	-236.3	

A similar comparison of the corresponding amyl ethers and esters (Guye and Chavanne, *loc. cit.*) leads to the same result:

	[M] _D	Difference.
l-Amyl ethyl ether, $\text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$	+0.7	2.5
l-Amyl benzyl ether, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$	+3.2	
l-Amyl acetate, $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$	+3.3	6.3
l-Amyl benzoate, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$	+9.6	

Both these cases involve change of residual affinity without any relative change of molecular position, and all show differences in rotatory power quite as marked as in the first-mentioned series, which involve progressive removal of an unsaturated radicle. Moreover, the examples of menthyl and amyl ethers display unmistakably the peculiar anomaly produced by conjugation, apart from any question of relative position in space.

It has been remarked (*Trans.*, 1908, **93**, 1618) that the sulphonic group SO_2 behaves as a relatively saturated group with reference to optical activity; use has been made of this fact to produce another series of comparisons bearing upon the present subject, in which, again without altering relative molecular positions, a conjugated system XY has been changed by replacing one member of the system ($\text{Y}\cdot\text{CO}$) by another of less residual affinity ($\text{Y}\cdot\text{SO}_2$), rather than by an almost completely saturated group ($\text{Y}\cdot\text{CH}_2$), as in the last examples. As the details given below demonstrate, in all cases the effect on optical activity is greatest in presence of the most unsaturated conjugated system, and when more than two systems are compared, the optical anomaly falls off in the same order as the residual affinities of the systems concerned.

The compounds studied in this way include, on the one hand, corresponding arylcarboxylic and arylsulphonic esters of menthol, and, on the other, the acetyl, benzoyl, and benzenesulphonyl derivatives of cinchonine and of cinchonidine.

The polarimetric measurements were carried out in chloroform solutions in a 2-dcm. tube maintained at a temperature of 13–14°.

Observations were made in the case of the menthyl esters with solutions containing 5 and 2.5 grams per 100 c.c. of solution respectively, and with solutions of 2 per cent. concentration of the alkaloidal derivatives. The results are summarised in the following tables:

I.—*Menthyl Esters.*

Ester.	C : 5.			C : 2.5.		
	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
Benzoate.....	-85.60	-222.6	+62.1	-86.04	-223.8	+62.6
Benzenesulphonate	72.68	215.1	54.6	73.20	216.7	55.5
<i>p</i> -Toluate	-95.22	-260.9	+100.5	-95.36	-261.3	+100.1
<i>p</i> -Toluenesulphonate.....	66.76	206.9	46.4	66.80	207.1	45.9
β -Naphthoate	-90.60	-280.9	+120.4	-91.12	-282.5	+121.3
Naphthalene- β -sulphonate.	56.50	195.4	34.9	57.12	197.6	36.4

II.—*Cinchonine Derivatives.*

Substituent.	C : 2.		
	$[\alpha]_D$.	$[M]_D$.	Difference.
Acetyl	+108.50	+364.6	—
Benzenesulphonyl	+62.15	+269.7	-94.9
Benzoyl	-27.80	-110.6	-475.2

III.—*Cinchonidine Derivatives.*

Acetyl	+12.90	+43.3	—
Benzenesulphonyl	+11.43	+49.6	+6.3
Benzoyl	+98.65	+392.6	+349.3

The conclusion is therefore reached that, in compounds where the influence of two or more given radicles on optical activity may be due either to their proximity to the asymmetric nucleus or to conjugated unsaturation, both causes contribute to the effect, but conjugation is evidently the predominating factor.

The series of brucine salts of aromatic ketonic acids given on a preceding page forms an excellent example of the combined effects of conjugation and of varying degrees of proximity of the unsaturated systems to the optically active group. Thus, when the acid group CO_2H remains attached to a carbonyl group, the anomaly is uniformly high, and is but slightly altered by successive removal of the phenyl group to more remote parts of the molecule, whilst the maximum exaltation occurs when there are two sets of conjugated systems in the molecule, although one of these is relatively distant from the asymmetric complex:

Brucine salt of:	$[M]_D$.	$[D]_D$.
Phenylglyoxylic acid, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CO}_2\text{H}$	-32.6	+214.8
Phenylpyruvic „ $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$	+20.4	267.8
Benzylpyruvic „ $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$	-54.9	192.5
Benzoylpyruvic „ $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$	+60.1	307.5

On the other hand, Rupe's explanation is plainly supported by those salts wherein the conjugated system $C_6H_5 \cdot CO$ is itself progressively separated from the optically active part of the molecule.

For instance, brucine β -phenylpropionate has an anomaly of 39.7, whilst that of the β -benzoylpropionate is 63.3:

Brucine salt of:	$[M]_D$	$[D]_D$
Phenylglyoxylic acid, $C_6H_5 \cdot CO \cdot CO_2H$	-32.6	+214.8
Benzoylacetic ,, $C_6H_5 \cdot CO \cdot CH_2 \cdot CO_2H$	180.0	67.4
β -Benzoylpropionic acid, $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$	184.1	63.3

EXPERIMENTAL.

Menthyl pyruvate, acetoacetate, and laevulate have already been described by Cohen and Whiteley (Trans., 1901, **79**, 1309), Lapworth and Hann (Trans., 1902, **81**, 1479), and McKenzie (Trans., 1905, **87**, 1380), but in order that all three might be examined under identical polarimetric conditions their preparation was repeated. The author's specimens possessed physical properties agreeing with those described by the above authors, and furnished satisfactory analytical numbers.

The brucine salts, except in a few stated cases, were directly made up from the equivalent amounts, accurately weighed, of the pure alkaloid and acid, dissolved in the corresponding quantity of chloroform, and then measured in the polariscope, after which they were recovered, crystallised, and analysed.

Brucine glyoxylate, $C_2H_4O_4, C_{23}H_{26}O_4N_2, 4H_2O$, was prepared by mixing roughly equivalent quantities of the acid (prepared as described by Perkin and Duppa, Trans., 1868, **21**, 197) and base in alcohol, precipitating by ether, and finally crystallising from a mixture of ether and alcohol. It formed a cream, micro-crystalline powder, which frothed at 160° , and decomposed at about 200° :

0.1049 gave 0.2083 CO_2 and 0.0654 H_2O . $C=54.14$; $H=6.93$.

$C_{25}H_{30}O_8N_2, 4H_2O$ requires $C=53.76$; $H=6.81$ per cent.

Brucine Pyruvate, $C_3H_4O_3, C_{23}H_{26}O_4N_2, 3H_2O$.—Soft, cream-coloured crystals, readily soluble in water, melting at 85° , and evolving H_2O at 105 — 110° :

0.1417 gave 0.3028 CO_2 and 0.0895 H_2O . $C=58.28$; $H=7.01$.

$C_{26}H_{30}O_7N_2, 3H_2O$ requires $C=58.21$; $H=7.09$ per cent.

Brucine acetoacetate, $C_4H_6O_3, C_{23}H_{26}O_4N_2, 4H_2O$, was prepared from the sodium salt of the acid and brucine hydrochloride in absolute alcohol, subsequently crystallising from a mixture of ether and alcohol. It appeared as a white, soft, crystalline powder, partly melting at 147 — 150° :

0.1880 gave 0.3950 CO_2 and 0.1178 H_2O . $C=57.30$; $H=6.96$.

$C_{27}H_{32}O_7N_2, 4H_2O$ requires $C=57.04$; $H=7.04$ per cent.

Brucine Laevulate, $C_5H_8O_3, C_{23}H_{26}O_4N_2, 4H_2O$.—Very small, hard, white crystals, which melt sharply at 58° , froth up violently at 112 — 114° , and again leave a clear liquid:

0.1344 gave 0.2854 CO_2 and 0.0737 H_2O . $C=57.91$; $H=7.32$.

$C_{28}H_{34}O_7N_2, 4H_2O$ requires $C=57.73$; $H=7.22$ per cent.

Dibrucine Mesoxalate, $C_3H_4O_6, (C_{23}H_{26}O_4N_2)_2$.—A white, crystalline powder, showing no change in appearance below 250° :

0.1020 gave 0.2386 CO_2 and 0.0583 H_2O . $C=63.80$; $H=6.36$.

$C_{49}H_{56}O_{14}N_4$ requires $C=63.63$; $H=6.06$ per cent.

Dibrucine Oxalacetate, $C_4H_4O_5, (C_{23}H_{26}O_4N_2)_2, 2H_2O$.—Soft, white nodules from ethyl acetate, melting with much frothing at 163 — 166° :

0.1596 gave 0.3687 CO_2 and 0.0988 H_2O . $C=62.98$; $H=6.88$.

$C_{50}H_{56}O_{13}N_4, 2H_2O$ requires $C=62.76$; $H=6.28$ per cent.

Dibrucine acetonedicarboxylate, $C_5H_6O_5, (C_{23}H_{26}O_4N_2)_2, H_2O$, separates from benzene in large, transparent, cubical crystals, melting at 179 — 180° :

0.1551 gave 0.3655 CO_2 and 0.0905 H_2O . $C=64.27$; $H=6.48$.

$C_{51}H_{58}O_{13}N_4, H_2O$ requires $C=64.29$; $N=6.30$ per cent.

The necessary aromatic ketonic acids were obtained by methods devised by Claisen (*Ber.*, 1887, **20**, 655, 2196; 1888, **21**, 1131), Erlenmeyer (*Annalen*, 1892, **271**, 163), Perkin (*Trans.*, 1884, **45**, 178), and Fittig (*Ber.*, 1896, **29**, 2582), and the purity of each was controlled by determination of the melting point.

Brucine Phenylglyoxylate, $C_8H_6O_3, C_{23}H_{26}O_4N_2, H_2O$.—Colourless, stable crystals, by ethereal precipitation of the alcoholic solution; the salt decomposes, but does not melt at 230° :

0.1112 gave 0.2697 CO_2 and 0.0636 H_2O . $C=66.15$; $H=6.36$.

$C_{31}H_{32}O_7N_2, H_2O$ requires $C=66.19$; $H=6.05$ per cent.

Brucine Phenylpyruvate, $C_9H_8O_3, C_{23}H_{26}O_4N_2, 2\frac{1}{2}H_2O$.—A cream-coloured salt, melting and decomposing at 182 — 183° :

0.1190 gave 0.2774 CO_2 and 0.0685 H_2O . $C=63.57$; $H=6.40$.

$C_{32}H_{34}O_7N_2, 2\frac{1}{2}H_2O$ requires $C=63.68$; $H=6.46$ per cent.

Brucine Benzylacetate, $C_9H_8O_3, C_{23}H_{26}O_4N_2, 5\frac{1}{2}H_2O$.—Colourless, slender needles, readily soluble in water, melting and decomposing at 196° :

0.1216 gave 0.2600 CO_2 and 0.0776 H_2O . $C=58.30$; $H=7.09$.

$C_{32}H_{34}O_7N_2, 5\frac{1}{2}H_2O$ requires $C=58.43$; $H=6.85$ per cent.

Brucine Benzylpyruvate, $C_{10}H_{10}O_3, C_{23}H_{26}O_4N_2, 5H_2O$.—A colourless, crystalline powder, melting at 100 — 103° :

0.1093 gave 0.2405 CO_2 and 0.0670 H_2O . $C=60.01$; $H=6.81$.

$C_{33}H_{36}O_7N_2, 5H_2O$ requires $C=59.81$; $H=6.95$ per cent.

Brucine β -Benzoylpropionate, $C_{10}H_{10}O_3, C_{23}H_{26}O_4N_2, 3H_2O$. — A cream-coloured, deliquescent, micro-crystalline powder, evolving water, and fusing at $101-103^\circ$:

0.1071 gave $0.2472 CO_2$ and $0.0660 H_2O$. $C=62.94$; $H=6.85$.

$C_{33}H_{36}O_7N_2, 3H_2O$ requires $C=63.35$; $H=6.71$ per cent.

Brucine Benzoylpyruvate, $C_{10}H_8O_4, C_{23}H_{26}O_4N_2, 2\frac{1}{2}H_2O$. — Hard, colourless tablets, losing water at 100° , melting and decomposing at 174° :

0.1126 gave $0.2587 CO_2$ and $0.0678 H_2O$. $C=62.66$; $H=6.69$.

$C_{33}H_{34}O_8N_2, 2\frac{1}{2}H_2O$ requires $C=62.76$; $H=6.18$ per cent.

Some of the amine salts employed in this work could not be obtained crystalline, or, at all events, sufficiently non-deliquescent for characterisation. Others, however, were definitely crystalline, and can be reported upon:

Di-n-butylamine Camphorate, $C_{10}H_{16}O_4(C_4H_9NH_2)_2$. — Delicate, white needles, melting at $150-152^\circ$:

0.1130 gave $0.2608 CO_2$ and $0.1111 H_2O$. $C=63.17$; $H=10.91$.

$C_{18}H_{38}O_4N_2$ requires $C=62.94$; $H=10.98$ per cent.

n-Butylamine Camphor- π -sulphonate,

$C_{10}H_{15}O \cdot SO_3H, C_4H_9NH_2, 1H_2O$.

—Wax-like, shining crystals, melting at 125° :

0.1204 gave $0.2342 CO_2$ and $0.1000 H_2O$. $C=53.06$; $H=9.25$.

$C_{14}H_{27}O_4NS, 1H_2O$ requires $C=53.31$; $H=9.22$ per cent.

Di-n-butylamine Tartrate, $C_4H_6O_6(C_4H_9NH_2)_2$. — Cream, deliquescent prisms, melting at $70-75^\circ$:

Dianiline Camphorate, $(C_6H_7N)_2, C_{10}H_{16}O_4, 1\frac{1}{2}H_2O$. — White, amorphous powder, softening at $255-260^\circ$:

0.1436 gave $0.3534 CO_2$ and $0.0906 H_2O$. $C=67.11$; $H=7.11$.

$C_{22}H_{30}O_4N_2, \frac{1}{2}H_2O$ requires $C=66.83$; $H=7.85$ per cent.

Diquinoline Camphorate, $(C_9H_7N)_2, C_{10}H_{16}O_4, 2H_2O$. — Deliquescent, crystalline mass, melting at $75-80^\circ$:

0.1226 gave $0.3046 CO_2$ and $0.0766 H_2O$. $C=67.76$; $H=6.94$.

$C_{28}H_{25}O_4N_2, 2H_2O$ requires $C=68.01$; $H=6.88$ per cent.

Di- α -naphthylamine Camphorate, $(C_{10}H_9N)_2, C_{10}H_{16}O_4, 2\frac{1}{2}H_2O$. — Small needles, turning reddish-purple in the air, and melting at 183° :

0.1180 gave $0.2938 CO_2$ and $0.0827 H_2O$. $C=67.90$; $H=7.79$.

$C_{30}H_{34}O_4N_2, 2\frac{1}{2}H_2O$ requires $C=67.79$; $H=7.35$ per cent.

α -Naphthylamine Camphor- π -sulphonate, $C_{10}H_9N, C_{10}H_{15}O_4S$. — Small, colourless flakes, turning blue-violet in the air, and melting at $194-196^\circ$:

0.1154 gave 0.2727 CO₂ and 0.0658 H₂O. C = 64.45; H = 6.34.

C₂₀H₂₅O₄NS requires C = 64.00; H = 6.37 per cent.

ar-Tetrahydro-α-naphthylamine Camphor-π-sulphonate,

C₁₀H₁₃N, C₁₀H₁₆O₄S, 4½H₂O.

—Glistening, colourless crystals, turning dark blue in the air, and melting somewhat indefinitely at 128—132°:

0.1053 gave 0.2016 CO₂ and 0.0854 H₂O. C = 52.22; H = 8.49.

C₂₀H₂₉O₄NS, 4½H₂O requires C = 52.17; H = 8.26 per cent.

β-Naphthylamine Camphor-π-sulphonate, C₁₀H₉N, C₁₀H₁₆O₄S.—A cream-coloured, micro-crystalline powder, melting indefinitely at 118—121°:

0.1304 gave 0.2620 CO₂ and 0.0707 H₂O. C = 54.80; H = 6.03.

C₂₀H₂₅O₄NS, 3½H₂O requires C = 54.80; H = 5.84 per cent.

Dianiline Tartrate, (C₆H₇N)₂, C₄H₆O₆.—A soft, crystalline powder, turning pink in the air, but colourless again on heating; melts and decomposes at 184—185°:

0.1128 gave 0.2028 CO₂ and 0.0660 H₂O. C = 49.05; H = 6.50.

0.0631 lost 0.0086 at 100°. H₂O = 13.63.

C₁₆H₂₀O₆N₂, 3H₂O requires C = 49.22; H = 6.67;

H₂O = 13.85 per cent.

Dipyridine Tartrate, (C₅H₅N)₂, C₄H₆O₆.—Crisp, colourless flakes, melting at 158°:

0.1152 gave 0.2112 CO₂ and 0.0582 H₂O. C = 49.99; H = 5.39.

C₁₄H₁₆O₆N₂, 1½H₂O requires C = 50.16; H = 5.67 per cent.

Diquinoline Tartrate, (C₉H₇N)₂, C₄H₆O₆.—A brick-coloured, crystalline powder, melting at 131°:

0.1093 gave 0.2142 CO₂ and 0.0551 H₂O. C = 53.44; H = 5.60.

C₂₂H₂₀O₆N₂, 5H₂O requires C = 52.99; H = 6.03 per cent.

Ditetrahydroquinoline Tartrate, (C₉H₁₁N)₂, C₄H₆O₆.—Crisp, cream-coloured flakes, turning green in air, and melting and decomposing at 118—120°.

Dibenzylamine camphorate, (C₇H₇·NH₂)₂, C₁₀H₁₆O₄, ½H₂O, forms crisp, colourless crystals, melting at 188—189°:

0.1162 gave 0.2907 CO₂ and 0.0983 H₂O. C = 68.21; H = 8.05.

C₂₄H₃₄O₄N₂, ½H₂O requires C = 68.10; H = 8.25 per cent.

Benzylamine camphor-π-sulphonate crystallised in slightly pink scales, darkening, without melting, at 230°.

Dibenzylamine tartrate, (C₇H₇·NH₂)₂, C₄H₄O₆, consists of small, colourless needles, melting at 112°:

0.1100 gave 0.2263 CO₂ and 0.0678 H₂O. C = 56.10; H = 6.85.

C₁₈H₂₄O₆N₂ requires C = 56.54; H = 6.81 per cent.

Menthyl Esters of Corresponding Aromatic Carboxylic and Sulphonic Acids.

The carboxylic esters have already been described by Tschugaeff (*loc. cit.*); the samples of these compounds prepared by the author possessed melting points in agreement with Tschugaeff's data.

The sulphonic esters were prepared from the respective acid chlorides and menthol in the cold in the presence of pyridine, as recommended by Patterson and Frew (*Trans.*, 1906, **80**, 332), who have described the benzene- and β -naphthalene-sulphonates of menthol. These esters are excellently adapted for polarimetric work, since they crystallise especially well, and are thus very easily and certainly purified.

Menthyl p-Tolylsulphonate, $C_7H_7 \cdot SO_3 \cdot C_{10}H_{19}$.—Long, hard, stout, colourless needles, sparingly soluble in cold alcohol, and melting at 97° :

0.1418 gave 0.3424 CO_2 and 0.1105 H_2O . $C = 65.80$; $H = 8.66$.

0.1292 „ 0.0950 $BaSO_4$. $S = 10.09$.

$C_{17}H_{26}O_3S$ requires $C = 65.80$; $H = 8.39$; $S = 10.32$ per cent.

Acyl Derivatives of Cinchonine and Cinchonidine.

The *acetyl* compounds, $CH_3 \cdot CO \cdot C_{19}H_{21}ON_2$, were prepared by heating the alkaloids on the water-bath with excess of acetic anhydride for two hours. After cooling, the reaction mixture was poured into water and rendered alkaline with dilute sodium hydroxide. The products were then isolated by extraction with ether, and purified from unchanged base by solution in a large amount of boiling light petroleum, which was finally removed under diminished pressure at the ordinary temperature, leaving the compounds in the form of cream-coloured, amorphous powders:

Acetylcinchonine melted at $51-53^\circ$:

0.1138 gave 0.3118 CO_2 and 0.0716 H_2O . $C = 74.73$; $H = 6.99$.

$C_{21}H_{24}ON_2$ requires $C = 75.01$; $H = 7.14$ per cent.

Acetylcinchonidine melted at $47-49^\circ$:

0.1602 gave 0.4400 CO_2 and 0.0992 H_2O . $C = 74.88$; $H = 6.90$.

The benzoyl derivatives, $C_6H_5 \cdot CO \cdot C_{19}H_{21}ON_2$, resulted when 3 parts of the alkaloid and 5 parts of benzoyl chloride were boiled together in benzene solution for two hours. The product appeared as an oily hydrochloride, from which the benzene was removed by decantation and repeated washing with ether. The salt was then dissolved in cold water, and excess of ammonia added. The liberated base, after being filtered and dried, was usually rendered pure by one or two crystallisations from ether.

The *benzenesulphonyl* compounds, $C_6H_5 \cdot SO_2 \cdot C_{19}H_{21}ON_2$, were obtained in a precisely similar manner from equal weights of benzenesulphonyl chloride and cinchonine or cinchonidine.

Benzoylcinchonine crystallises in hard nodules from light petroleum or ether, but is too soluble in benzene or alcohol to crystallise well therefrom at the usual temperature. It melts somewhat indefinitely at $104-105^\circ$:

0.1574 gave 0.4510 CO_2 and 0.0982 H_2O . $C=78.14$; $H=6.93$.

$C_{26}H_{26}O_2N_2$ requires $C=78.39$; $H=6.54$ per cent.

Benzoylcinchonidine separates from ether in small, hard needles, soluble in alcohol, insoluble in light petroleum, melting to a clear liquid at 183° :

0.1040 gave 0.2992 CO_2 and 0.0621 H_2O . $C=78.47$; $H=6.64$.

Benzenesulphonylcinchonine crystallises from ether, but is almost insoluble in benzene:

0.1223 gave 0.3089 CO_2 and 0.0669 H_2O . $C=68.88$; $H=6.08$.

$C_{25}H_{26}O_3N_2S$ requires $C=69.11$; $H=5.99$ per cent.

Benzenesulphonylcinchonidine may be obtained from a boiling benzene solution as small needles, melting at 166° :

0.1924 gave 0.4896 CO_2 and 0.1080 H_2O . $C=69.37$; $H=6.24$.

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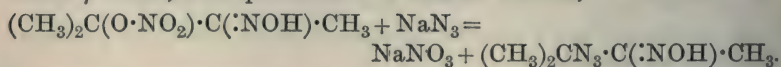
XXVIII.—*The Triazo-group. Part XVI. Interaction of Nitrosates and Sodium Azide.*

By MARTIN ONSLOW FORSTER and FREDERIK MARINUS VAN GELDEREN.

THE aliphatic azoimides which have been studied hitherto are derived from the corresponding halogen derivatives by double decomposition with sodium azide, a method of production which renders the azoimide nucleus comparable with the typical groups of the aliphatic nitriles, nitro-compounds, and carbimides. The fact that nitrosates, such as those of amylene and the terpenes, are capable of exchanging the nitroxyl group for NHX when treated with amines, giving rise to nitrolamines, led us to anticipate the

possibility of converting them into "nitrosoazides" by the action of sodium azide.

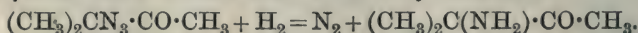
Our first experiments have been carried out with the nitrosate of isoamylene or trimethylethylene, originally prepared by Guthrie (*Annalen*, 1860, **116**, 248), and later by Wallach (*Annalen*, 1888, **245**, 243), who showed that potassium cyanide in aqueous alcohol transforms it into the nitrile of ketoximinodimethylacetic acid, an operation repeated by J. Schmidt (*Ber.*, 1902, **35**, 3726). On warming a suspension of the freshly prepared nitrosate in an alcoholic-aqueous solution of sodium azide, we found that the nitrosate is readily converted into the corresponding triazo-compound, "trimethylethylene nitrosoazide," or β -triazobutanol- γ -oxime, with production of sodium nitrate,



The triazo-oxime obtained in this way, unlike the material from which it is produced, is unimolecular, and is readily hydrolysed to the corresponding triazoketone, $(\text{CH}_3)_2\text{CN}_3\cdot\text{CO}\cdot\text{CH}_3$, which differs from earlier members of this class in the condition of the azoimide nucleus, since this is attached to a tertiary carbon atom. Comparison with triazocamphor (*Trans.*, 1905, **87**, 826), triazoacetone (*Trans.*, 1908, **93**, 81), and the triazo-derivatives of methyl ethyl ketone (*loc. cit.*, p. 675) shows that whilst these compounds, in which the triazotised carbon atom is either primary or secondary, lose approximately two-thirds the azidic nitrogen when treated with alcoholic sodium ethoxide, this agent acts quite differently on β -triazobutanol- γ -one, which, although ultimately yielding nitrogen and ammonia, does so as the result of a profound alteration accompanied by the development of an intense, blood-red coloration; the oxime, however, is converted into a mixture of the unsaturated

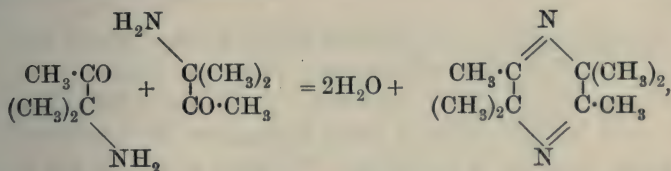
oximes, $\begin{matrix} \text{CH}_2 \\ \text{CH}_2 \end{matrix} \gg \text{C}\cdot\text{C}(\text{:NOH})\cdot\text{CH}_3$, unaccompanied by elemental nitrogen. Thus, the triazoketone establishes very clearly the principle suggested by the behaviour of triazomethylacetoacetic and triazoethylacetoacetic esters towards alkali (*Trans.*, 1910, **97**, 1360), namely, the dependence of the triazotised carbon atom upon hydrogen for the change first brought to light by the behaviour of camphorylazoimide towards alkali.

Early in the investigation it was recognised that the new triazoketone might prove to be a convenient source of β -amino- β -methylbutanol- γ -one, which should arise from it by reduction:



The well-known work of Gabriel on aminoketones has shown that such substances readily undergo intermolecular condensation, yield-

ing pyrazine derivatives, but the comparative stability of α -amino-camphor, coupled with the absence of hydrogen from the carbon atom associating the carbonyl and amino-groups in the above aminobutanone, led us to hope that it might resist the family tendency. Experiment showed, however, that although it is possible to produce the aminoketone in the form of a benzoyl derivative or salts, attempts to set it free from the latter by alkali led to hexamethyldihydropyrazine,



which forms a very characteristic hexahydrate, melting at 86—87°, and subliming with unusual readiness. It is not necessary for us to proceed with a description of this compound, however, because there has just appeared a communication by Gabriel (*Ber.*, 1911, **44**, 57), according to which the same substance is produced by combining phthaliminoisobutyryl chloride with ethyl sodiomalonate and hydrolysing the product with hydriodic acid.

The interaction of trimethylethylene nitrosate and sodium azide suggested the possibility of converting terpenoid nitrosites and nitrosates into triazo-oximes which might be less easily obtained by other methods, and experiments in this direction, leading to dipentene nitrosoazide, will be described later. Moreover, since it is the nitroxyl group which lends itself to exchange, it should be possible to convert the nitric esters of aliphatic alcohols into the corresponding alkyl azoimides by interaction with sodium azide, and this we have found practicable in the case of *isoamyl* nitrate, which is converted, although with some difficulty, into *isoamyl* azoimide. Very recently it has been observed by Meldola and Kuntzen (this vol., p. 36) that an aromatic nitro-group in 2:3:5-trinitro-4-acetylaminophenol may be exchanged for an azoimide nucleus.

EXPERIMENTAL.

β -Triazo- β -methylbutan- γ -oxime (Trimethylethylene Nitrosoazide), $(\text{CH}_3)_2\text{CN}_3 \cdot \text{C}(\text{CH}_3) : \text{NOH}.$

Three hundred grams of amylene nitrosate, prepared from 430 c.c. (292 grams) of trimethylethylene, were divided into quantities of 10 grams; each portion was covered with 30 c.c. of alcohol, mixed with 4.5 grams of sodium azide in the minimum quantity of water, and heated gently until the appearance of bubbles indicated action,

which was then allowed to proceed spontaneously. As a result of shaking and occasionally warming, the crystals slowly disappeared, forming a clear solution which at no stage was green or blue, and after an interval of twelve hours the accumulated liquid, containing crystals of sodium nitrate, was diluted largely with crushed ice, which precipitated lustrous, snow-white plates. The product was filtered and distilled in steam, yielding 94 grams of the solid oxime, a further quantity of which was obtainable from the mother liquor:

0.1617 gave 56.6 c.c. N_2 and 22° and 758 mm. $N=39.40$.

$C_5H_{10}ON_4$ requires $N=39.44$ per cent.

The triazo-oxime melts at $34-35^\circ$. It is freely soluble in organic media, and crystallises from ether in massive, transparent plates; hot water dissolves it sparingly. The cold substance has a faint odour of peppermint, but in steam the vapour has a pungent, overpowering odour, and exerts the worst physiological effects of the more volatile azoimides. Aqueous alkali neither dissolves it nor removes hydroxylamine, but the latter change is readily brought about by cold dilute sulphuric acid. With concentrated sulphuric acid the substance does not liberate gas until vigorously stirred, but with stannous chloride in hydrochloric acid effervescence quickly becomes brisk. A determination of molecular weight by depression of the freezing point gave the mean value 159 instead of 127. The benzoyl derivative is an oil.

Reduction.—On passing hydrogen sulphide into an alcoholic solution of the nitrosoazide rendered alkaline with ammonia, nitrogen was gradually liberated; when this change was complete, the liquid was evaporated, acidified with dilute sulphuric acid, filtered from sulphur, and shaken with benzoyl chloride in presence of sodium hydroxide. The solid product, after crystallisation from dilute methyl alcohol, melted at 142° , the temperature observed by Wallach for the dibenzoyl derivative of amylene nitrolamine (*Annalen*, 1891, **262**, 332).

β -Triazo- β -methylbutan- γ -one, $(CH_3)_2CN_3 \cdot CO \cdot CH_3$.

Forty-five grams of the triazo-oxime were heated under reflux with 100 c.c. of 10 per cent. sulphuric acid on the water-bath during two to three hours, and the product extracted with ether; the residue from this was treated in the same way, and the operation repeated until the aqueous liquid failed to reduce cold Fehling's solution. The substance was then distilled under diminished pressure, 30 grams being obtained:

0.1440 gave 41.7 c.c. N_2 at 18° and 744 mm. $N=33.25$.

$C_5H_9ON_3$ requires $N=33.07$ per cent.

The triazoketone is a colourless liquid, having a pleasant, refreshing, peppermint-like perfume distinct from that of methyl ethyl ketone. It boils at $42^{\circ}/14$ mm., and decomposes without exploding at 170 — 180° under atmospheric pressure; the density is $1.0057/18^{\circ}$. The action with concentrated sulphuric acid and with stannous chloride is vigorous, but the substance is not affected by cold dilute alkali; if boiled with Fehling's solution, however, reduction takes place, accompanied by liberation of gas, and an odour of isocyanide.

The *semicarbazone*, $(\text{CH}_3)_2\text{CN}_3\cdot\text{C}(\text{:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_3$, was prepared in the usual manner, and crystallised from benzene in rosettes of lustrous, colourless needles, melting at 127° :

0.1284 gave 51.0 c.c. N_2 at 21° and 754 mm. $\text{N}=45.75$.

$\text{C}_6\text{H}_{12}\text{ON}_6$ requires $\text{N}=45.65$ per cent.

The substance is readily soluble in cold chloroform and hot benzene, but boiling water or petroleum dissolves it sparingly, the former depositing six-sided prisms; it is indifferent towards alkali, and is rapidly hydrolysed by dilute hydrochloric acid.

The *thiosemicarbazone*, $(\text{CH}_3)_2\text{CN}_3\cdot\text{C}(\text{:N}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2)\cdot\text{CH}_3$, arose on heating 2 grams of thiosemicarbazide in 50 per cent. alcohol with a slight excess of the triazoketone during two hours under reflux; on evaporating the solvent, there remained an oil which solidified when scratched. The product, weighing 3 grams, was dissolved in 7 c.c. of hot benzene, which deposited transparent, six-sided prisms, melting at 106 — 107° :

0.1386 gave 50.8 c.c. N_2 at 16° and 756 mm. $\text{N}=42.33$.

$\text{C}_6\text{H}_{12}\text{SN}_6$ requires $\text{N}=42.00$ per cent.

It is freely soluble in cold chloroform, but dissolves sparingly in hot petroleum; boiling water dissolves it more readily than the semicarbazone, and deposits long, lustrous needles as it cools. The thiosemicarbazone is quickly hydrolysed by cold dilute hydrochloric acid.

Reduction of the Triazoketone.

Numerous attempts were made to reduce β -triazo- β -methylbutan- γ -one, with the object of studying the corresponding aminoketone, but, as already stated, we have been anticipated in this branch of the investigation by Gabriel (*loc. cit.*). Aluminium amalgam in ether, stannous chloride in hydrochloric acid, alcoholic ammonium sulphide, and zinc dust in acetic acid, all led to the characteristic hexahydrate of hexamethyldihydropyrazine, which is conveniently isolated in the form of the picrate. Of these processes the last-named was the most suitable, 2 grams of the triazoketone being dissolved in 20 c.c. of 50 per cent. acetic acid, and treated with

2 grams of zinc dust, added in very small quantities while the liquid was cooled; each addition of metal produced general effervescence throughout the liquid, which remained clear when the liberation of nitrogen was complete. Subsequent treatment consisted in adding excess of alkali, and passing steam through the liquid or extracting it with chloroform, which deposited the product in lustrous plates on spontaneous evaporation.

Our observations on the pyrazine derivative bear out in every respect those of Gabriel, and it is therefore superfluous to give a detailed description of the substance. The hexahydrate, which melts at $86-87^{\circ}$ (Gabriel gives $88-89^{\circ}$), has a pronounced, menthol-like odour, and sublimes freely in brilliant, transparent, quadratic prisms; after two or three days in the desiccator, the powdered substance was found to have changed into lustrous crystals of different geometrical form, melting incompletely at $50-52^{\circ}$. The picrate, on account of its sparing solubility in cold alcohol, is useful in recognising small quantities of the base; 2 grams, dissolved in 225 c.c. of boiling alcohol, separated in long, lustrous, sulphur-yellow prisms, melting at 230° after becoming deep red:

0.1206 gave 18.9 c.c. N_2 at 17.5° and 740.5 mm. $N=17.93$.

$C_{10}H_{18}N_2 \cdot C_6H_3O_7N_3$ requires $N=17.72$ per cent.

The platinichloride is insoluble in water, alcohol, acetone, and ethyl acetate, but was recrystallised from hot alcohol containing hydrochloric acid, which deposited small, transparent, pale red prisms, remaining solid at 310° ($Pt=33.73$; $C_{10}H_{20}N_2Cl_6Pt$ requires $Pt=33.86$ per cent.).

With the object of preparing the aminoketone, the triazoketone was reduced with stannous chloride in hydrochloric acid, hydrogen sulphide being used to precipitate the tin; on adding alkali to the filtrate, and shaking with benzoyl chloride, the product melted at 125° , the temperature recorded by Gabriel.

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XXIX.—*The Triazo-group. Part XVII. Nitrosoazides of Pinene and Terpeneol.*

By MARTIN ONSLOW FORSTER and SIDNEY HERBERT NEWMAN.

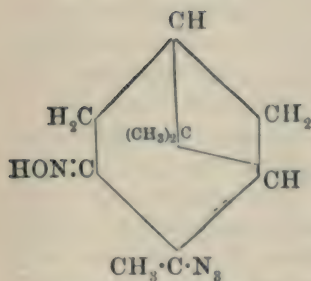
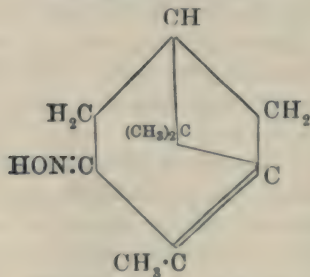
DURING the thirty-five years which have elapsed since pinene nitrosochloride was characterised by Tilden, the substance itself, and the reaction upon which it is based, have continued to furnish data of interest and importance to the chemistry of the terpene

series. Early in the history of the nitrosochlorides, it was found that whilst the action of sodium ethoxide withdraws the elements of hydrogen chloride, treatment with a primary aliphatic amine involves an exchange of chlorine for the substituted ammonia residue, the products being called nitrolamines. Variations of this reaction have been described by Tilden and Burrows (*Trans.*, 1905, **87**, 344), Tilden and Leach (*Trans.*, 1904, **85**, 931), Leach (*Trans.*, 1907, **91**, 1), and Cusmano (*Gazzetta*, 1910, **40**, ii, 122), as the results of which pinene nitrosocyanide, the limonene nitrosocyanides, pinene nitrolamine, and pinene hydroxylamineoxime, respectively, have been brought to light. The general applicability of this reaction suggested the possibility of introducing the triazo-group into the pinene nucleus by the action of sodium azide on the nitrosochloride, and we find that this change may be brought about very easily, the yield of nitrosoazide leaving little to be desired.

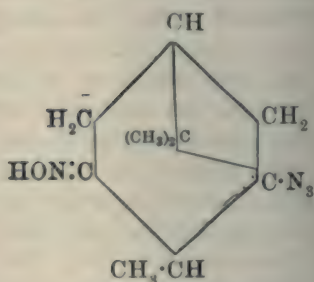
Pinene nitrosoazide is a unimolecular substance, melting at 120° , dissolving readily in organic media, and distilling slowly in steam. Alcoholic sodium ethoxide quickly removes the elements of hydrazoic acid, forming nitrosopinene, but the analogy to the nitrosochloride does not extend to the action of piperidine, for this base also produces nitrosopinene instead of the nitrolpiperidide, behaving, in fact, like diethylamine with the nitrosochloride. This indication of the presence of an *isonitroso*-group is confirmed by the production of an acetyl derivative (m. p. 64°), but on attempting to convert the nitrosoazide into the triazoketone, as prescribed by Wallach (*Annalen*, 1906, **346**, 220) for the isolation of carvopinone from nitrosopinene, namely, hydrolysis with aqueous oxalic acid, it was found that hot water alone gives rise to an isomeric pinene nitrosoazide, melting at 126° , and yielding an acetyl derivative which melts at 71° . Two possibilities present themselves as an explanation of this change, either inversion of the carbon atom which carries the methyl and triazo-groups, or transference of the latter to a neighbouring atom, similar to the rearrangement which takes place when hydrogen chloride converts pinene into bornyl chloride. We believe that the latter alternative underlies the transformation in question. Although it is true that sodium ethoxide withdraws hydrazoic acid from the isomeric pinene nitrosoazide (m. p. 126°), thereby producing nitrosopinene, the following formulæ made it clear that the latter might arise from an isomeride differing in structure from the original pinene nitrosoazide (m. p. 120°). As, moreover, the action of hot water on the isomeride involves disruption of the tetramethylene ring, and leads to the oxime of hydroxydihydrocarvone with elimination of hydrazoic acid, it is natural to conclude that

it is one of the carbon atoms involved in this disruption which carries the azoimide nucleus; interchange of the latter with a methyl group being precluded, the representation we suggest seems the most probable:

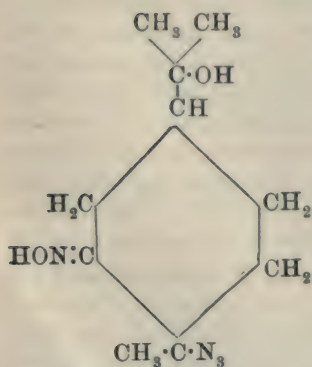
Nitrosopinene: m.p. 131°.



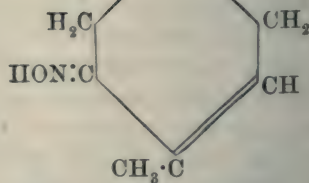
Pinene nitrosoazide;
m.p. 120°.



Pinene nitrosoazide;
m.p. 126°.



Terpineol nitrosoazide;
m. p. 111°.



Hydroxydihydrocarvoxime;
m.p. 133·5°.

The terpeneol nitrosoazide represented above was prepared from inactive terpeneol, melting at 35° , by converting it into the nitrosochloride, and acting on this with alcoholic-aqueous sodium azide. Thus the hydroxydihydrocarboxime obtained from it by the action of sodium ethoxide is inactive also, and is identical with the specimen produced from the isomeric pinene nitrosoazide (m. p. 126°).

Progress has been made in the extension of this reaction to other nitrosochlorides, including those of limonene, and the results will be described later.

EXPERIMENTAL.

Pinene Nitrosoazide, $C_{10}H_{15}(:NOH) \cdot N_3$.

Fifty grams of freshly prepared pinene nitrosochloride were suspended in 250 c.c. of 84 per cent. alcohol containing 24 grams of sodium azide, and gently warmed; at the first sign of action, the flask was withdrawn from the steam-bath, and allowed to remain at about 40° during one hour. This treatment was repeated throughout the day, when it was found that the nitrosochloride had passed into solution, leaving a suspension of sodium chloride; the liquid was then diluted with water until crystallisation began. At no time was a blue or green colour noticed, and an occasional test for free hydrazoic acid gave only the faintest indication of that substance. The filtered product, which weighed 40 grams, was recrystallised from hot alcohol, then from a mixture of benzene and petroleum, and finally from benzene alone, 4 grams requiring about 15 c.c. of the hot solvent, which deposited brilliant, colourless, transparent prisms, melting to a colourless liquid at 120° :

0.2122 gave 0.4474 CO_2 and 0.1490 H_2O . $C = 57.50$; $H = 7.87$.

0.0950 „ 22.0 c.c. N_2 at 18° and 767 mm. $N = 27.13$.

$C_{10}H_{16}ON_4$ requires $C = 57.63$; $H = 7.74$; $N = 26.92$ per cent.

The substance is freely soluble in cold ethyl acetate, chloroform, acetone, and hot benzene or alcohol, less readily in boiling petroleum. It is insoluble in 15 per cent. potassium hydroxide, and the solution in concentrated sulphuric acid effervesces only slowly on being stirred vigorously; with stannous chloride in hydrochloric acid, however, liberation of nitrogen takes place more actively. In steam the nitrosoazide is somewhat volatile, the vapour having a terpenoid and pungent odour, producing the disagreeable throbbing effect in the head which is so characteristic of the aliphatic azoimides. A determination of molecular weight by depression of the freezing point of benzene gave the mean value 227, $C_{10}H_{16}ON_4$ requiring 208.

Conversion into Nitrosopinene.—The nitrosoazide was heated under reflux with alcohol in which one atomic proportion of sodium

had been dissolved, precipitation of sodium azide taking place very rapidly. After three hours the liquid was poured into water, which precipitated nitrosopinene, identified with a specimen prepared from the nitrosochloride. The same substance, melting at 131° , was obtained by the action of piperidine in hot alcohol, this base failing to yield the nitrolpiperidide, which melts at $118-119^{\circ}$.

The Acetyl Derivative.—On heating pinene nitrosoazide with acetic anhydride during a few hours on the steam-bath, water precipitated a material which was recrystallised twice by diluting a solution in warm acetic acid:

0.1212 gave 23.2 c.c. N_2 at 20° and 774 mm. $N = 22.23$.

$C_{12}H_{18}O_2N_4$ requires $N = 22.41$ per cent.

The substance is very freely soluble in organic media, even petroleum, from which it separates in aggregates of tough, transparent, rectangular prisms, melting at 64° .

The Isomeric Pinene Nitrosoazide (m. p. 126°).

On subjecting a considerable quantity of the nitrosoazide (m. p. 120°) to steam distillation, it was noticed that the solid distillate, even after recrystallisation, melted very indefinitely at $80-100^{\circ}$, whilst the residual liquid deposited lustrous, colourless needles, melting at 133.5° , and no longer containing the triazo-group. Accordingly, 10 grams were heated under reflux during six hours on the steam-bath with about 100 c.c. of water and sufficient alcohol to ensure the return of the volatile nitrosoazide to the flask; a current of steam then carried over 3.5 grams of a colourless solid, accompanied by a considerable proportion of hydrazoic acid, whilst the hot aqueous residue yielded about 3 grams of the substance melting at 133.5° . The distillate was recrystallised three times from hot petroleum, in which it is more readily soluble than the original nitrosoazide, forming lustrous, transparent, six-sided prisms, melting at 126° :

0.1818 gave 0.3838 CO_2 and 0.1284 H_2O . $C = 57.57$; $H = 7.90$.

0.1361 „ 31.3 c.c. N_2 at 17° and 764 mm. $N = 26.84$.

$C_{10}H_{16}ON_4$ requires $C = 57.63$; $H = 7.74$; $N = 26.92$ per cent.

Thus the product appears to be isomeric with the original material, the melting point of which was depressed to about 100° by admixture. The presence of the triazo-group was revealed by effervescence with concentrated sulphuric acid and a hydrochloric acid solution of stannous chloride. The cold substance has a distinct, terpenoid colour, which becomes very pronounced in steam. A determination of molecular weight by depression of the freezing point of benzene gave the mean value 224, $C_{10}H_{16}ON_4$ requiring 208.

Action of Alcoholic Sodium Ethoxide.—Two grams were heated

under reflux with 15 c.c. of alcohol, in which 0.3 gram of sodium had been dissolved, and having been poured into water after two hours, rendered faintly acid with acetic acid. The precipitate was crystallised first from alcohol, then from petroleum, when it melted at 131° , and did not depress the melting point of nitrosopinene when mixed with it.

The Acetyl Derivative.—Three grams of the isomeride of pinene nitrosoazide (m. p. 126°) were heated with 10 c.c. of acetic anhydride during three hours on the steam-bath; the solid obtained on dilution was crystallised twice from dilute acetic acid, and finally from hot petroleum, which deposited aggregates of brittle, transparent plates, melting at 71° ; a mixture of this product with the isomeric acetyl derivative (m. p. 64°) became liquid at about 50° :

0.1284 gave 24.0 c.c. N_2 at 18° and 781 mm. $N=22.20$.

$C_{12}H_{18}O_2N_4$ requires $N=22.41$ per cent.

The substance is very freely soluble in organic media.

Action of Hot Water.—Two grams of the nitrosoazide (m. p. 126°) were heated under reflux with water and a small quantity of alcohol during six hours, when a current of steam was passed through the liquid; 1.1 gram of unchanged material was carried over, along with hydrazoic acid, whilst the residual liquid deposited lustrous needles identical with the above-mentioned by-product melting at 133.5° . This was found on analysis to have the composition $C_{10}H_{17}O_2N$:

0.1649 gave 0.3976 CO_2 and 0.1431 H_2O . $C=65.77$; $H=9.70$.

0.2273 „ 15.4 c.c. N_2 at 17° and 759 mm. $N=7.85$.

$C_{10}H_{17}O_2N$ requires $C=65.57$; $H=9.37$; $N=7.65$ per cent.

We were thus led to suspect identity with the oxime of hydroxy-dihydrocarvone, stated by Wallach to melt at $133-134^{\circ}$, and on preparing the diacetyl derivative from our product, this melted at 107° , the temperature recorded by Wallach for that substance. The presence of the oximino-group was further indicated by the action of hot dilute sulphuric acid, which eliminated hydroxylamine.

The Benzoyl Derivative.—By the action of benzoyl chloride in 10 per cent. sodium hydroxide, a monobenzoyl derivative was produced:

0.2194 gave 9.8 c.c. N_2 at 17° and 764 mm. $N=5.12$.

$C_{17}H_{21}O_3N$ requires $N=4.88$ per cent.

It melts at $83-84^{\circ}$ after crystallisation from a mixture of benzene and petroleum.

Terpineol Nitrosoazide, $C_{10}H_{16}(OH)(\cdot NOH) \cdot N_3$.

Thirteen grams of nitrosochloride, prepared from inactive terpineol (m. p. 35°), were suspended in 100 c.c. of 84 per cent. alcohol, and allowed to remain with 6 grams of sodium azide at about 40° until the suspended material consisted of sodium chloride. This occupied a few hours, and did not involve change of colour or liberation of hydrazoic acid. On pouring the product into water, terpineol nitrosoazide separated as an oil which solidified very slowly, the first crop weighing 5 grams; a further quantity separated from the mother liquor in the course of another week. The product was moistened with cold petroleum, drained on earthenware, and recrystallised twice from the minimum quantity of hot benzene, which deposited clusters of small, transparent, six-sided plates, melting at 111° :

0.1717 gave 0.3337 CO_2 and 0.1244 H_2O . $C=53.01$; $H=8.11$.

0.0952 „ 20.2 c.c. N_2 at 19° and 779 mm. $N=25.01$.

$C_{10}H_{18}O_2N_4$ requires $C=53.05$; $H=8.02$; $N=24.80$ per cent.

The substance is freely soluble in organic media, excepting petroleum, which dissolves it sparingly on boiling; it is also somewhat soluble in cold water, crystallising slowly in long, six-sided prisms. The nitrosoazide is odourless, even in boiling water, but the azidic character is revealed by effervescence with concentrated sulphuric acid and a hydrochloric acid solution of stannous chloride. When heated with alcoholic sodium ethoxide, sodium azide is precipitated, and hydroxydihydrocarboxime is formed (m. p. 133.5°).

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XXX.—*New Derivatives of d-Glucosamine.*

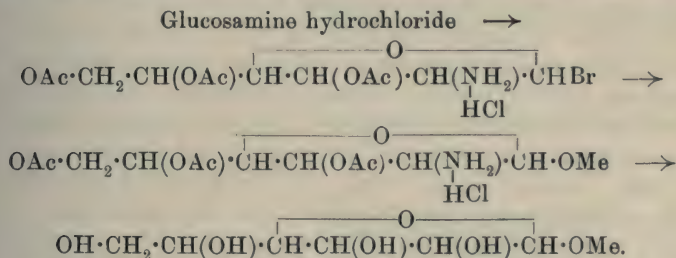
By JAMES COLQUHOUN IRVINE, DAVID McNICOLL, M.A., B.Sc. (Carnegie Scholar), and ALEXANDER HYND, M.A., B.Sc. (Carnegie Scholar).

THE action of acetyl bromide on reducing sugars, by means of which the latter are converted into aceto-halogen derivatives, has recently been extended considerably by Fischer and his pupils (*Ber.*, 1909, **42**, 2776; 1910, **43**, 2521). Owing to their convenient solubilities, the ready displacement of the halogen atom, and the ease with which the acetyl groups may be subsequently eliminated, these acetylated

bromo-compounds are likely to prove of great service in sugar synthesis. In particular, the preparation by Fischer of non-reducing disaccharides by self-condensation of acetylated aldoses opens up a new field in the formation of sugar complexes.

Towards the close of 1908 a research was commenced in this laboratory on the constitution of glucosamine, and the paper published by one of us, "A Polarimetric Method of Identifying Chitin" (Trans., 1909, **95**, 564), contained some results which were obtained in the early part of the work. The action of acetyl bromide on glucosamine hydrochloride was subsequently undertaken with the object of preparing a bromotriacetylglucosamine from which a triacetylmethylglucosamine could be obtained. Presumably a glucoside of this nature would, owing to the absence of hydroxyl groups, react normally with nitrous acid, and thus be converted ultimately into methyl glucoside. Additional evidence of a peculiarly direct nature would thus be obtained as to the relationship between glucosamine and glucose.

The theoretical steps in the scheme of reactions is shown below:



The experimental difficulties encountered have delayed the completion of the research on the above lines, and, during the progress of the work, important papers have been published by Fischer on the application of acetyl bromide as a reagent in the sugar group. Owing to the similarity of the methods employed by us, we considered it advisable to submit our results to Professor Fischer so as to avoid duplication, and, in a private communication, he kindly informed us in advance of the details of his recent research on amino-sugars (*Ber.*, 1911, **44**, 132). The investigation in question includes the preparation of an aminomethylglucoside, which, in his opinion, does not appear to be a derivative of glucosamine, and as our work has now resulted in the formation of an aminoglucoside which is possibly identical with Fischer's, we have arranged to publish our results simultaneously and in a less complete form than otherwise would be desirable.

We find that glucosamine hydrochloride reacts with acetyl bromide to give bromotriacetylglucosamine hydrobromide (m. p.

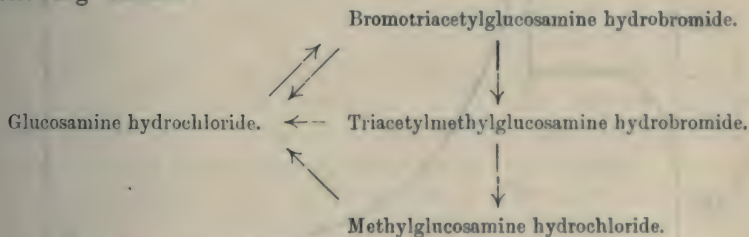
149—150°, $[\alpha]_D + 148.4^\circ$). The salt-forming molecule of hydrogen chloride originally present is thus displaced by hydrogen bromide, but otherwise the reaction is normal, and the primary amino-group is not affected by the reagent. The product displays the usual properties of an aceto-halogen sugar derivative. When dissolved in moist acetone, hydrogen bromide is formed, and, in the absence of a base, the acetyl groups are slowly eliminated, so that glucosamine hydrobromide is finally produced. The conversion into a "methylglucoside" was effected by dissolving the bromo-compound in methyl alcohol containing one molecular proportion of pyridine, the product of the change being triacetylmethylglucosamine hydrobromide (m. p. 230—233°, $[\alpha]_D + 20.26^\circ$). This compound behaved as a glucoside towards Fehling's solution, and contained one methoxyl group. The action of nitrous acid on the substance confirmed the presence of the amino-group, but the acetyl groups were also eliminated during the reaction, and, so far, no definite derivative of glucose has been isolated from the products.

The hydrolysis of triacetylmethylglucosamine hydrobromide, when carried out with concentrated hydrochloric acid, resulted in the formation of glucosamine hydrochloride, but the hydrolysis may be controlled so that only the acetyl groups are removed, while the glucosidic methoxyl group remains unaltered. This was effected by boiling with barium hydroxide in aqueous solution and also by the prolonged action of a 0.75 per cent. methyl-alcoholic solution of hydrogen bromide in the cold. In either case, a non-acetylated aminomethylglucoside results, which, in the meantime, may be termed *methylglucosamine*. The compound reacts strongly basic, and forms a well-defined hydrochloride (m. p. 185°), which gives $[\alpha]_D - 19.5^\circ$ in aqueous solution. It has no action on Fehling's solution until after hydrolysis, and reacts as an amino-compound towards nitrous acid. The latter reaction has, so far, only been carried out on the small scale, but we intend to examine the products of the change with the object, if possible, of isolating methylglucoside.

The aminomethylglucoside recently prepared by Fischer from dibromotriacetylglucose (*loc. cit.*) shows many similarities with that just described, but it is difficult in the meantime to say definitely if the compounds are isomeric or identical. It is important to arrive at a decision on this point, as, assuming the compounds to be identical, a direct synthesis of glucosamine from glucose is thus established by Fischer. A comparison of the two compounds is therefore included in the discussion which follows. In the course of the work, triacetylglucosamine hydrobromide and a dibarium derivative of glucosamine were isolated as by-products.

*Discussion of Results.**Constitution and Nomenclature of the Compounds Described.*

As, in addition to the correlation of glucosamine and glucose, the object of the present research is the synthesis of complexes containing the glucosamine residue, it is important that the constitution of the compounds involved should be established. Each substance has accordingly been hydrolysed, and the products have been identified. This was considered necessary in view of the fact that, in the decomposition of bromotriacetylglucosamine, pyridine was used to remove hydrogen bromide, and, in the subsequent preparation of methylglucosamine, silver carbonate was employed for the same purpose. Neither reagent seems, however, to have occasioned intramolecular changes, as all the compounds described gave either glucosamine hydrobromide or hydrochloride on complete hydrolysis. This definite relationship to glucosamine is therefore embodied in the nomenclature used, and is shown in the following scheme:



Each of the new derivatives should, like the parent substance, exist in α - and β -modifications, and, in the case of bromotriacetylglucosamine, the two forms should be spontaneously interconvertible. This was confirmed by examination of solutions in anhydrous non-hydroxy-solvents, optical changes then resulting which were not due to decomposition, and which must therefore be regarded as normal mutarotation. The change was difficult to detect, as minute traces of moisture decompose the bromo-compound and give rise to apparent mutarotation, but the following result shows that the compound is precipitated from solution in a labile form.

Solvent: Pure dry acetone. $c = 5.01$.

Time from first reading.	$[\alpha]_D^{20^\circ}$.
0 minutes	+ 135.9°
60 "	143.9
90 "	148.4 (approximately constant)

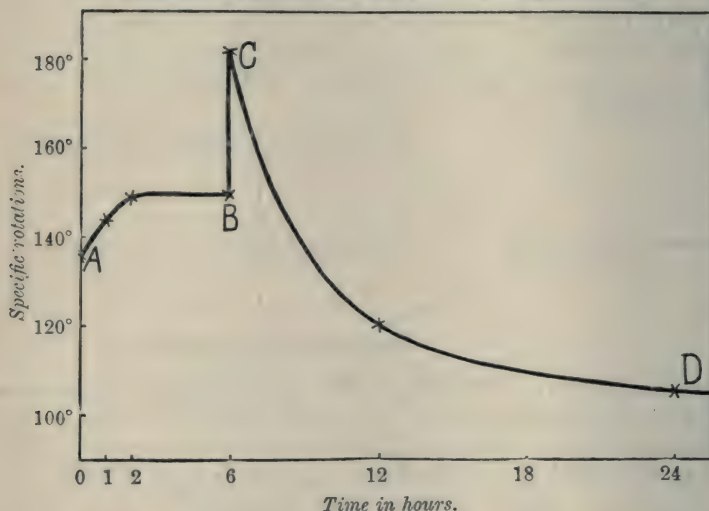
The equilibrium solution was then diluted to half the concentration with acetone containing 2 per cent. of water. The

specific rotation at once increased to $+181.6^\circ$, and then diminished gradually, as shown below :

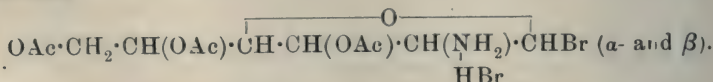
Specific rotation before addition of aqueous acetone.....	+ 148.4°
“ “ after “ “ “ “ “ “ ..	181.6
“ “ 12 hours later.....	120.9
“ “ 36 “ “ ..	94.3
“ “ 240 “ “ ..	44.0

A crystalline substance gradually separated, from the third day onwards, until finally nothing remained in solution. This product, when recrystallised from methyl alcohol, was shown to be glucosamine hydrobromide. The interpretation of the optical changes is simplified by plotting the values in a curve :

Rotation changes observed during the conversion of bromotriacetylglucosamine hydrobromide into glucosamine hydrobromide.

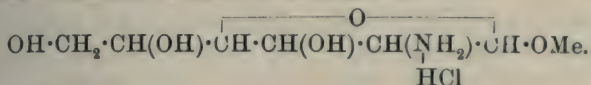


Normal mutarotation in the pure solvent is represented by *AB*, the immediate formation of triacetylglucosamine by the sharp rise *BC*, whilst *CD* represents the gradual removal of the acetyl groups and the precipitation of the product from solution. From these considerations, we regard the bromo-compound as possessing the structure :



Considering the method employed in the preparation of a methylglucoside from the above compound, the product should be the β -form. This is supported by the low value of the specific rotation,

and by the fact that different preparations gave uniformly the same result. On the other hand, inspection of the experimental details will show that our preparation of methylglucosamine probably consists of a mixture of the α - and β -forms:



This complicates comparison with Fischer's aminomethylglucoside hydrochloride. The solubilities and crystalline forms of the two substances are similar, but whilst Fischer's compound gives $[\alpha]_{\text{D}} -25.1^\circ$ and decomposes at 210° , we find that methylglucosamine hydrochloride gives $[\alpha]_{\text{D}} -19.5^\circ$, and melts indefinitely at $185-187^\circ$. These differences might, however, be explained on the assumption that the two preparations are mixtures of α - and β -forms in different proportions, the melting point in one case being lowered below the decomposition point. A more serious point of apparent distinction is the behaviour of the compounds towards hydrolytic agents. Fischer's aminoglucoside is hydrolysed by *N*-hydrogen chloride at 100° to give a product other than glucosamine hydrochloride. On the other hand, we find that methylglucosamine is only hydrolysed to a slight extent by similar treatment. Even after heating for two hours at 100° with 10 per cent. hydrochloric acid, only a slight rise of rotatory power in the dextro-sense was evident, and, as rotatory changes during the hydrolysis of glucosides are usually well marked, we conclude that the change is imperfect under the given conditions. It should be stated, however, that, during the action, the liquid acquired a very decided action on Fehling's solution, and the product, when isolated, no longer behaved definitely as a glucoside. The use of concentrated hydrochloric acid as the hydrolytic agent gave, however, a normal result, the specific rotation rapidly altering from -17° to $+52^\circ$, and glucosamine hydrochloride was then isolated in nearly quantitative amount from the solution. It would thus appear that the glucosidic group in methylglucosamine is either remarkably stable, or that the hydrolysis of the compound is accompanied by the formation of intermediate complexes, which are only decomposed into glucosamine hydrochloride by concentrated acid. It is also conceivable that, if hydrolysed polarimetrically with concentrated acid, Fischer's compound may similarly give the glucosamine salt. This, as already pointed out, would be a highly desirable result.

EXPERIMENTAL.

Preparation of Glucosamine Hydrochloride.

The starting material used was chitin, which was prepared from lobster shells in the usual way. The product was not precipitated, and was therefore in the massive state. The conversion into the glucosamine salt by boiling with hydrochloric acid results in some decomposition, but we have succeeded in increasing the yield considerably by carrying out the hydrolysis according to the method described by one of us for polarimetric experiments (*loc. cit.*). As the economical preparation of glucosamine hydrochloride is important, we submit the details of one typical experiment.

Fifty grams of dry chitin were vigorously shaken in a wide-mouthed bottle with 1250 c.c. of concentrated hydrochloric acid for six hours. A clear, syrupy solution was thus obtained, and the hydrolysis was completed by heating at 50° for an additional period of six hours, the liquid being vigorously stirred during the process. The solution, which was only slightly brown, was then concentrated nearly to dryness at 50°/15 mm. Absolute alcohol (150 c.c.) was then added, and the crude glucosamine salt collected. The product, when recrystallised in the usual manner, amounted to 80 per cent. of the weight of chitin used, and no gummy by-products were formed. A quantity of 200 grams of the glucosamine salt, prepared by the above process, was used in the following experiments.

Bromotriacetylglucosamine Hydrobromide.

In the preparation and manipulation of this compound, all the materials used must be specially dried, and precautions taken to exclude moisture. As the action of acetyl bromide on glucosamine hydrochloride is vigorous, and the bromoaceto-derivative formed is decomposed by the reagent, the best conditions for the preparation of the compound were only ascertained after a large number of experiments had been made. The reaction must be carried out with small quantities of material, and, in order to avoid the necessity to weigh out the reagent, the best method is to use in each preparation the weight of glucosamine salt corresponding with the weight of acetyl bromide contained in a tared sealed bottle. The following are the details of one typical preparation. 8.4 Grams of glucosamine hydrochloride (1 mol.) were introduced into a boiling tube fitted with a reflux condenser and provided with a mechanical stirrer working in a mercury seal. Twenty-five grams (5 mols.) of acetyl bromide were then added, and the well-stirred mixture cautiously heated. Reaction usually commenced at 60°, and

hydrogen bromide was steadily evolved for thirty minutes, after which the mixture suddenly solidified. The tube, when cold, was broken in a mortar, the hard mass roughly powdered, and kept in a vacuum desiccator over soda-lime until free from hydrogen bromide. The yield of crude material thus obtained was almost the theoretical amount, and no unchanged glucosamine hydrochloride remained.

The use of a larger proportion (9 mols.) of acetyl bromide than that recommended above is inadvisable, as the product remains in solution, and no definite end-point to the reaction can be detected, as hydrogen bromide is continuously evolved owing to decomposition of the product. The use of the theoretical amount of the reagent is also inconvenient, as about 20 per cent. of the glucosamine salt escapes reaction. It was also impossible to carry out the reaction successfully in chloroform solution, as apparently triacetylglucosamine hydrobromide resulted.

The crude bromo-compound was dissolved in hot chloroform, filtered from traces of glucosamine salts, and the solution allowed to evaporate spontaneously until crystals formed on the side of the crystallising basin. After the addition of a small quantity of dry ether, the solution was vigorously stirred, and in a few minutes the purified compound suddenly separated. When pure, bromotriacetylglucosamine hydrobromide consists of colourless, delicate needles, softening at 144° , and melting and decomposing at $149-150^{\circ}$. The compound is readily soluble in water, methyl or ethyl alcohols, acetone or ethyl acetate, reacting with the hydroxy-solvents, but is insoluble in ether or hydrocarbons:

Found, C = 32.05; H = 4.47; Br = 34.66; N = 3.17.

$C_{12}H_{18}O_7NBr \cdot HBr$ requires C = 32.08; H = 4.28; Br = 35.62;
N = 3.12 per cent.

Unless specially purified, the compound rapidly acquired a pink colour, but a pure specimen has now remained colourless for several months.

Permanent specific rotation in acetone ($c = 5.01$)	+ 148.4°
" " " ethyl acetate ($c = 1.096$)	+ 152.8

The above values gradually diminished after some time, owing to hydrolysis.

Triacetylmethylglucosamine Hydrobromide.

A 5 per cent. solution of bromotriacetylglucosamine hydrobromide was prepared in absolute methyl alcohol containing 1 per cent. of anhydrous pyridine. Optical examination of the filtered liquid showed that the reaction was complete after six hours at

the laboratory temperature, and that the reaction is quantitative. The solvent was removed at $20^{\circ}/15$ mm., and the residue crystallised from methyl alcohol containing a small quantity of ether. Access of moisture during all the operations must be carefully excluded, as otherwise the deliquescence of the pyridine salt results in the formation of syrupy products. A small quantity of glucosamine hydrobromide is also produced, and the yield of the pure glucoside isolated does not exceed 52 per cent. of the theoretical amount:

Found, C=38.94; H=5.83; Br=20.10; N=3.70; OMe=7.50.

$C_{12}H_{18}O_7N(OMe),HBr$ requires C=38.99; H=5.55; Br=19.97; N=3.50; OMe=7.74 per cent.

Triacetylmethylglucosamine hydrobromide crystallises in delicate prisms, melting and completely decomposing at $230-233^{\circ}$. The compound is readily soluble in water or alcohol, sparingly so in acetone, insoluble in ethyl acetate, chloroform, ether, or benzene. The aqueous solution reacts feebly acid to litmus, and behaves as a glucoside towards Fehling's solution. Ammonia is evolved when the compound is boiled with sodium hydroxide, the solution turning brown.

Solvent.	c.	Specific rotation.
Methyl alcohol.....	2.098	+20.26° (without mutarotation)
Water	1.240	20.56 " "

Hydrolysis of Triacetylmethylglucosamine Hydrobromide.

Complete Hydrolysis by Hydrogen Chloride.—A 5 per cent. solution in concentrated hydrochloric acid was kept for twelve hours at 20° . During this time the specific rotation diminished from $+25.5^{\circ}$ to -6° , owing to the removal of the acetyl groups. The solution was then heated in boiling water, polarimetric readings being taken at intervals. The rotation rapidly became dextro, and after forty minutes the value was $[\alpha]_D +16^{\circ}$. Thereafter the liquid suddenly turned brown, so that no further optical examination was possible. The solvent was removed at $30^{\circ}/15$ mm., the residue washed with alcohol, and recrystallised from water by the addition of alcohol. The product reduced Fehling's solution, gave the nitrous acid test, and was shown to be glucosamine hydrochloride by determination of the specific rotation and halogen content:

Found, $[\alpha]_D^{20^{\circ}}$ in water $+89.6^{\circ} \rightarrow 71.5^{\circ}$; Cl=16.55 per cent.

Glucosamine hydrochloride requires $[\alpha]_D^{20^{\circ}} \rightarrow 72.5^{\circ}$.

Cl=16.44 per cent.

Partial Hydrolysis by Barium Hydroxide.—3.3 Grams of triacetylmethylglucosamine hydrobromide were dissolved in 100 c.c. of an aqueous solution of barium hydroxide containing 7.84 grams $Ba(OH)_2 \cdot 8H_2O$, and the liquid was boiled under a condenser for

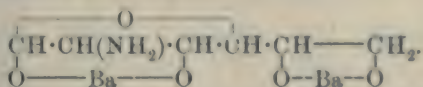
forty-five minutes. The equivalent amount of *N*-sulphuric acid was then added, and, after removing the barium sulphate, the solution was evaporated at 30°/15 mm. The solid residue was extracted in the first place with boiling ethyl alcohol, and afterwards with cold methyl alcohol. The former extract gave, on evaporation, a syrup which reduced Fehling's solution. This was dissolved in excess of methyl alcohol containing 0.25 per cent. of hydrogen chloride, and heated at 90° for twelve hours. The acid was removed by means of silver carbonate, and the filtrate, on evaporation in a vacuum, yielded a syrup which reacted as a strong base. On dissolving in cold concentrated hydrochloric acid and precipitating with excess of acetone, a crystalline precipitate was obtained. This proved to be the hydrochloride of methylglucosamine which is subsequently described.

The methyl-alcoholic extract described above, when decolorised and evaporated, yielded a semi-crystalline residue. After drying on porous porcelain and recrystallisation from methyl alcohol, the product was found to be free from halogen, but contained barium. Analysis of a specimen dried at 100° gave:

Found, C=14.14; H=1.93; Ba=61.41.

$C_6H_9O_5NBa_2$ requires C=16.00; H=2.01; Ba=61.10 per cent.

Owing to the small quantity of material available for combustion, the analytical values are only approximate, but, taken in conjunction with the barium estimation, indicate that the compound possesses the structure:



As it is unlikely that the glucosidic methoxyl group would be removed by the alkali, the above product seems to have resulted from impurities present in the glucoside used. Similar compounds have been obtained by Fischer in the hydrolysis of acetylated sugars, and the general stability of these barium derivatives is remarkable.

Partial Hydrolysis by Hydrogen Bromide.—A 5 per cent. solution of the glucoside salt in water containing 2 per cent. of hydrogen bromide was heated for several hours at 50°. The optical change was very slight, indicating slow removal of the acetyl groups. At 80° the action was more rapid, the specific rotation diminishing in three hours from +19.5° to -6.5°. The acid was removed by means of silver carbonate, the free base isolated as already described, and converted into the hydrochloride. The same product was obtained free from action on Fehling's solution by dissolving tri-acetylmethylglucosamine hydrobromide in methyl alcohol containing 0.75 per cent. of hydrogen bromide, and keeping the solution in the

dark until the rotation became constant. The optical change was complete in about twenty days, the product being converted into the hydrochloride as described above. The method of slow hydrolysis obviates the necessity to remove traces of reducing sugars by condensation with methyl alcohol.

Action of Nitrous Acid.—The reaction was carried out by shaking an alcoholic or aqueous solution of the hydrobromide with silver nitrite. In the former case the evolution of nitrogen was slow and the decomposition of the amino-group imperfect, but in aqueous solution the reaction appeared to proceed normally. The isolation of the product was carried out by the method adopted by Fischer, but in each case it was found that the acetyl groups had been partly removed, and that the syrup obtained reduced Fehling's solution actively. Attempts to convert the mixed products into a glucoside or into a definite hexose have so far been unsuccessful, but the properties of the syrup differ from those of chitose, and the reaction is being repeated.

Methylglucosamine Hydrochloride.

This compound, when prepared by the methods already described, crystallises in needles melting and decomposing at 185—187°. Analysis of a specimen dried at 95° gave:

Found, C=36.17; H=7.17; Cl=15.09; OMe=12.57.

$C_6H_{12}O_4N(OMe),HCl$ requires C=36.58; H=7.02; Cl=15.44;
OMe=13.51 per cent.

Methylglucosamine hydrochloride is readily soluble in water or methyl alcohol, and behaves as a glucoside towards Fehling's solution. Nitrogen is evolved on the addition of nitrous acid, and ammonia is disengaged when the compound is boiled with sodium hydroxide, the liquid turning brown. The compound apparently exists in α - and β -modifications, as different preparations showed a variation in melting point and specific rotation:

M. p. 187°.	Solvent: methyl alcohol.	$c=2.581.$	$[\alpha]_D^{20} - 16.7^\circ$	(no mutarotation).
„ 180°.	„ „ „	$c=2.150.$	$[\alpha]_D^{20} - 13.95$	„ „
„ 180°.	„ water	$c=3.892.$	$[\alpha]_D^{20} - 19.5$	„ „

As our preparation may not be a pure stereochemical form, the above values are liable to subsequent correction.

Hydrolysis of Methylglucosamine Hydrochloride.

Complete Hydrolysis by Hydrogen Chloride.—A 2.046 per cent. solution of the glucoside salt in concentrated hydrochloric acid was heated in boiling water for fifteen minutes. The specific rotation altered from -17° to $+52^\circ$, and the liquid turned brown. The

hydrolysis was then complete, as glucosamine hydrochloride in similar concentration and similarly dissolved gives $[\alpha]_D + 52^\circ$ (*loc. cit.*). The solvent was removed at $30^\circ/15$ mm., and the crystalline residue of glucosamine hydrochloride purified as usual:

Found, $[\alpha]_D^{20^\circ} + 94.4^\circ \rightarrow 71.7^\circ$. Cl = 16.71 per cent.

Glucosamine hydrochloride requires $[\alpha]_D^{20^\circ} \rightarrow 72.5^\circ$.

Cl = 16.44 per cent.

Action of Dilute Hydrochloric Acid.—A 1.5 per cent. solution of methylglucosamine hydrochloride in water containing 5 per cent. of hydrogen chloride was heated for two hours at 100° . The optical change then observed was $[\alpha]_D - 18.3^\circ \rightarrow -17.7^\circ$. The concentration of acid was then increased to 10 per cent., and the solution heated for three hours in boiling water. During the treatment with even the more dilute acid, the solution acquired a decided action upon Fehling's solution, but with the higher concentration of acid the optical change was only $[\alpha]_D - 17.7^\circ \rightarrow +7.3^\circ$, and apparently only 25 per cent. of the glucoside was hydrolysed. The product, isolated as usual, resembled the original material, melted indefinitely at 172° , reduced Fehling's solution strongly, and gave $[\alpha]_D - 5^\circ$ in methyl-alcoholic solution. Owing to lack of material, we were unable to confirm our idea that the reducing action was due to the presence of a small quantity of glucosamine hydrochloride. The ready solubility of the product in methyl alcohol is not against this assumption, as it is possible to obtain a 0.892 per cent. solution of glucosamine hydrochloride in methyl alcohol. It is thus evident that the method of purification employed, namely, solution in methyl alcohol and precipitation with ether, would only give a pure product when carried out on a scale sufficiently large to permit of fractional precipitation.

The research is being continued on the lines indicated in this communication.

The authors take the opportunity of expressing their indebtedness to the Carnegie Trust for a grant in aid of the investigation, and of expressing their appreciation of the courtesy shown them by Professor Emil Fischer.

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XXXI.—*The Interaction of Silver Nitrate and Potassium Persulphate and its Catalytic Effect in the Oxidation of Organic Substances.*

By PERCY CORLETT AUSTIN.

WHEN aqueous solutions of silver nitrate and potassium persulphate are mixed, a black precipitate is formed, of which no analysis has hitherto been published. This subject has already received attention by Marshall (*Proc. Roy. Soc. Edin.*, 1900, **23**, 163), and by Marshall and Inglis (*ibid.*, 1902, **24**, 88). The assumption was made that silver persulphate is first formed, and that this rapidly decomposes with water according to the equation:



At the suggestion of Professor Inglis, I have investigated this product, and have also studied the catalytic effect produced by adding a trace of silver nitrate to aqueous solutions of potassium persulphate in the presence of organic substances. A study of the results obtained by careful analysis indicates the correctness of the above assumption, the black precipitate consisting of a mixture of silver peroxide, silver persulphate, and water, in proportions which varied somewhat, according to the conditions under which it was prepared. The appended results were all obtained from the same specimen.

In the preparation of the precipitate for analysis, various proportions were tried, the best results being obtained by using about two molecules of potassium persulphate to one of silver nitrate. Owing to the sparing solubility of potassium persulphate in water, the solutions employed were necessarily very dilute. The dilution used was also sufficient to prevent the separation of silver sulphate, the presence of which was at one time suspected.

Ten grams of silver nitrate dissolved in 100 c.c. of distilled water were added to a solution of 30 grams of potassium persulphate in a litre of water, at the ordinary temperature, in a large separating funnel, the mixture being thoroughly shaken. The formation of the black precipitate, although not immediate, quickly followed. Owing to the difficulty of filtering such a solution, since the persulphate attacks filter-paper, it was kept for about an hour, by which time the bulk of the precipitate had settled and could be drawn off. It was immediately shaken with distilled water, washed three or four times by decantation; and finally filtered and washed again. It was then spread out on a watch-glass and dried in a vacuum desiccator over sulphuric acid. The drying was found to

require several days. The substance was indeed allowed to remain thus for some weeks, when it was transferred to a stoppered weighing bottle, and kept in a desiccator. Owing to its hygroscopic nature, it could not be weighed on an open watch-glass. The substance was then analysed.

Heating it in a crucible gave unsatisfactory results, since it decomposes explosively at about 110° , and although several trials were made by heating it in covered crucibles in the air-oven, there was always a loss by spirting. A qualitative examination of the residue, which was soluble in nitric acid, showed the presence of a sulphate. This might have been originally present as such or as persulphate. The residue was also tested for nitrate by dissolving in sulphuric acid and applying the ferrous sulphate test. No trace of nitrate could be found. Eventually determinations were made of silver by conversion into silver chloride; of sulphur as sulphate; of the total oxygen obtained by ignition, and of water.

To estimate the silver and sulphur, a weighed quantity was boiled with dilute hydrochloric acid until no more chlorine was evolved, and the whole of the black substance disappeared. The solution was then found to contain sulphuric acid, which was precipitated and weighed as barium sulphate after the silver chloride had been transferred to a Gooch crucible. That all the silver was thus converted to chloride was certain, since the same result was obtained by dissolving the original substance in dilute nitric acid, and then adding hydrochloric acid. The latter method was, however, unsuitable for the precipitation of barium sulphate, which then followed. Water was determined by weighing the original substance in a porcelain boat and heating it in a current of dry air in a combustion tube, which was packed at each end with ignited asbestos to prevent scattering. The water was collected and weighed in a U-tube containing sulphuric acid.

The estimation of the total oxygen expelled on heating was carried out in the following way. A weighed quantity of the substance was mixed with dry sand, and heated in a Jena-glass test-tube attached to a Toepler pump. As it decomposes explosively on heating, the test-tube was well packed with asbestos to prevent spirting. Before heating, the air was exhausted, and after heating, the total oxygen was drawn off and measured. Attempts were also made to estimate the amount of "available" oxygen by treating known quantities with potassium iodide solution and dilute sulphuric acid, and titrating the liberated iodine with sodium thiosulphate. The results obtained were, however, very variable, and therefore untrustworthy, since the available oxygen did not react quantitatively under these conditions:

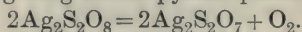
0.7477 gave 0.7804 AgCl and 0.1801 BaSO₄. Ag=78.57; SO₄=9.90.
 0.4970 „ 0.5179 AgCl „ 0.1203 BaSO₄. Ag=78.44; SO₄=9.95.
 0.4452 „ 0.4682 AgCl „ 0.1067 BaSO₄. Ag=79.14; SO₄=9.86.
 0.2646 „ 0.2772 AgCl. Ag=78.85.
 0.2682 „ 0.0068 H₂O. H₂O=2.53.
 0.2080 „ 15.65 c.c. O₂ (dry) at 15.1° and 764 mm. O=10.25.
 0.2561 „ 19.27 c.c. O₂ (dry) „ 14.7° „ 770 mm. O=10.34.

Mean: Ag=78.75; SO₄=9.90; H₂O=2.53; total oxygen expelled by heat=10.29 per cent.

Interpretation of the Results.

It may now be considered what light these results throw upon the constitution of the substance. That it is an oxidising agent is shown by its action on dilute hydrochloric acid, from which chlorine is liberated. Hence possible constituents are an oxide of silver, together with silver persulphate or silver sulphate. Now one would expect silver sulphate to remain unchanged on heating; hence the total oxygen expelled by heat would be derived from the oxide of silver. Theoretically, 9.90 grams of SO₄ require 22.23 grams of silver for the formation of silver sulphate. Therefore we should have 56.52 grams of silver combined with 10.29 grams of oxygen; expressed in percentages, this gives Ag=84.58; O=15.40. Hence the atomic ratio obtained, namely, 1: 1.228, is not a simple one.

On the other hand, if silver persulphate be present, it would lose oxygen on heating, giving silver pyrosulphate,



Now, 9.90 grams of SO₄ require 11.115 grams of silver to give 21.015 grams of silver persulphate, which, on heating, would lose 0.82 gram of oxygen. Hence, 78.75 - 11.12 = 67.63 parts of silver combine with 10.29 - 0.82 = 9.47 parts of oxygen; this gives Ag=87.7 and O=12.28 per cent., values which stand in the atomic ratio of 1.06: 1, thus corresponding fairly well with the formula Ag₂O₂.

Evidently the latter view is the more reasonable, and accords well with the assumption made by Marshall (*loc. cit.*).

Under these conditions the results may be tabulated thus:

Ag = 78.75	
S ₂ O ₇ = 9.08	[Ag ₂ S ₂ O ₇ being the final product on heating Ag ₂ S ₂ O ₈]
H ₂ O = 2.53	
Total oxygen = 10.29	
<hr/>	
100 65	

We may therefore conclude that the specimen analysed contained approximately: Ag₂S₂O₈=21; Ag₂O₂=77; H₂O=2.5 per cent.

Use of Silver Nitrate as a Catalytic Agent in Oxidations with Potassium Persulphate.

I. *Oxidation of Toluene.*—The catalytic effect of silver nitrate is very pronounced in this case. Two parallel experiments were made under similar conditions for the sake of comparison, using a trace of silver nitrate in one case only. In each experiment, 10 grams of potassium persulphate (3 mols.) were dissolved in 120 c.c. of slightly warm distilled water. One gram of toluene (1 mol.) was added, and in one case 5 c.c. of *N*/10-silver nitrate solution. (This quantity of water proved to be insufficient to retain all the potassium persulphate in solution on cooling.) The flasks were corked, well shaken, and allowed to remain. In the one containing silver nitrate, the liquid quickly became turbid, then yellow; soon a yellow oil separated. On the following day this was extracted with ether. On evaporation of the ether, a yellow oil was obtained, which reduced silver nitrate, giving a mirror, and had the odour of benzaldehyde. Benzoic acid was also formed and was extracted by shaking some of the ethereal solution with dilute sodium hydroxide, and acidifying. Crystals were obtained, which on recrystallisation from hot water melted at 119–120°.

In the other experiment, neither turbidity nor colour was observed, and on extracting with ether at the same time that the first was extracted, only unchanged toluene was found.

II. *Oxidation of Thymol.*

While the above experiments were in progress, a paper by Henderson and Boyd (*Trans.*, 1910, **97**, 1659) appeared, in which it was stated that the oxidation of thymol in alkaline solution by potassium persulphate led only to tarry products, the bulk of the substance remaining unchanged, whereas hydrogen peroxide gave tetrahydroxycymene. This experiment was repeated with the persulphate, omitting the alkali and adding a trace of silver nitrate. Forty grams of potassium persulphate were dissolved in two litres of slightly warm water, and introduced into a flask with 20 grams of finely powdered thymol and 5 c.c. of *N*/10-silver nitrate. The mixture was allowed to remain for several days with frequent shakings. After a few hours, the solid turned brown. (In a parallel experiment without silver nitrate, no change was observed until after several weeks.)

After about a week the liquid was filtered off, the residue well shaken with dilute sodium hydroxide and ether, and the layers separated. The alkaline solution was acidified, and the precipitate allowed to crystallise once from ether, in which it was very soluble.

It was then recrystallised two or three times from benzene, from which it separated in needles melting at 162° . This substance is readily soluble in ether, ethyl acetate, acetone, or alcohol, but less so in benzene. Analysis and a determination of its molecular weight by the ebullioscopic method showed it to be dithymol, a substance first prepared by Dianin (*J. Russ. Phys. Chem. Soc.*, 1882, **14**, 135). (Found, C=80.44; H=9.23. 0.2034, in 9.6 of ether, gave $E=0.16^{\circ}$. M.W.=286. Calc., C=80.53; H=8.72 per cent. M.W.=298.)

The ethereal solution of the portion insoluble in alkali was evaporated. A brown solid remained, for which no crystallising medium could be found. Although insoluble in cold aqueous sodium hydroxide, it dissolved partly on prolonged heating. To ensure a better effect, it was dissolved in alcohol; sodium hydroxide was then added, and the mixture heated on the water-bath for half an hour. Steam was then blown through to expel the alcohol, and the liquid was filtered. On acidifying the filtrate, a small quantity of dithymol was obtained. The residue was again treated in a similar manner until no more substance would dissolve in alkali. The remainder was a brown, amorphous powder, which is possibly a polymerisation product.

The use of silver nitrate as a catalyst in oxidations of organic substances of various types is being further investigated.

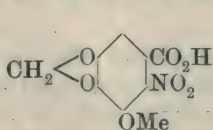
In conclusion, I desire to express my thanks to Professor Inglis for his kind interest in the work.

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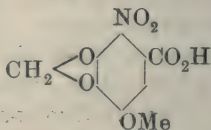
XXXII.—*The Orientation of the Nitro-Group in Nitro-myristicinic Acid.*

By ARTHUR HENRY SALWAY.

In a previous investigation (*Trans.*, 1909, **95**, 1165) it was shown that myristicinic acid is converted by the action of cold concentrated nitric acid into a mixture of 5-nitro-1-methoxy-2:3-methylenedioxybenzene and nitromyristicinic acid. The position of the nitro-group in the latter compound was not definitely established, there being two possible formulæ, as represented by I and II:



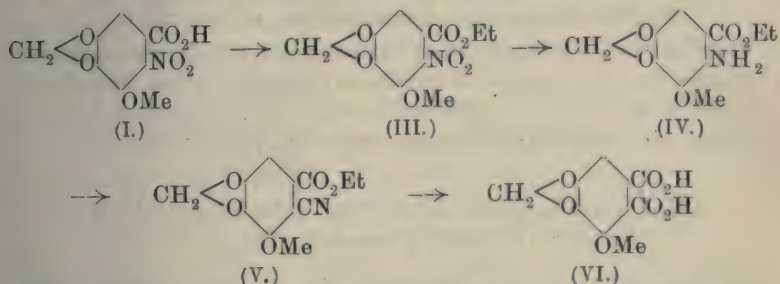
(I.)



(II.)

The present investigation was therefore undertaken with the object of ascertaining which of these formulæ must be assigned to the nitromyristicinic acid prepared in the above-mentioned reaction.

The method employed consisted in the conversion of the nitro-group of nitromyristicinic acid into a carboxylic group, when the product would be cotarnic acid (VI) or an isomeride, according as the constitution of nitromyristicinic acid is represented by formula I or II. This transformation was successfully accomplished according to the series of reactions represented below, and the final product was identified as cotarnic acid. Nitromyristicinic acid must therefore possess the constitution I, and is 6-nitro-5-methoxy-3:4-methylenedioxybenzoic acid:



The determination of the position of the nitro-group in nitromyristicinic acid establishes, in addition, the constitutions of nitromyristicinaldehyde (*loc. cit.*, p. 1160), and of a series of synthetic products derived from the latter compound * (Trans., 1909, 95, 1204).

EXPERIMENTAL.

For the purpose of this investigation it was necessary to prepare a considerable quantity of nitromyristicinic acid. The method already described for the preparation of this compound (Trans., 1909, 95, 1165) is unsatisfactory, since approximately 60 per cent. of the myristicinic acid is converted into 5-nitro-1-methoxy-2:3-methylenedioxybenzene by elimination of carbon dioxide. It has now been found, however, that by esterification of the myristicinic acid prior to nitration the secondary change is entirely avoided.

* These compounds comprise: ω -2-dinitro-3-methoxy-4:5-methylenedioxy-styrene; 2-nitro-3-methoxy-4:5-methylenedioxy-cinnamic acid; 2-amino-3-methoxy-4:5-methylenedioxy-cinnamic acid; 2-keto-8-methoxy-6:7-methylenedioxy-1:2-dihydroquinoline; 8-methoxy-6:7-methylenedioxy-carbostyryl methyl ether; 2-keto-8-methoxy-1-methyl-6:7-methylenedioxy-1:2-dihydroquinoline and oxyisocotarnine.

Ethyl Nitromyristicinate (*Ethyl 2-Nitro-3-methoxy-4:5-methylenedioxybenzoate*), III, p. 267.

Twenty grams of ethyl myristicinate (b. p. $193^{\circ}/20$ mm.) were added gradually at 0° to 200 c.c. of concentrated nitric acid (D 1.41). The mixture was kept in the cold for an hour, and then poured into ice-water, when an oil was precipitated, which gradually solidified. This was collected, washed free from nitric acid, and purified by recrystallisation from alcohol. The compound was thus obtained in stout, colourless prisms, melting at 82° :

0.4019 required for saponification 15.05 c.c. $N/10$ -NaOH.

Saponification value = 210.1.

$C_{11}H_{11}O_7N$ requires saponification value = 208.6.

Ethyl nitromyristicinate is colourless when freshly prepared, but gradually becomes yellow on exposure to light. When hydrolysed, it yields a mononitromyristicinic acid, which was proved to be identical with the acid derived by the direct nitration of myristicinic acid.

Ethyl Aminomyristicinate (*Ethyl 2-Amino-3-methoxy-4:5-methylenedioxybenzoate*), IV, p. 267.

For the preparation of this compound, one part of ethyl nitromyristicinate was cautiously heated with tin (one part) and an excess of concentrated hydrochloric acid. After the vigorous reaction had subsided and the nitro-ester had completely dissolved, the mixture was poured into a large volume of water, when the greater portion of the amino-ester was precipitated as an oil, which soon became solid. This was collected, washed, and purified by recrystallisation from alcohol. A further quantity of the amino-ester was obtained from the acid filtrate by rendering it alkaline and extracting with ether:

0.1114 gave 0.2250 CO_2 and 0.0546 H_2O . $C=55.1$; $H=5.4$.

$C_{11}H_{13}O_5N$ requires $C=55.2$; $H=5.4$ per cent.

Ethyl aminomyristicinate crystallises from alcohol in colourless, prismatic needles, melting at 93° . Its ethereal solution possesses a blue fluorescence. It is a very weak base, being precipitated from its solution in concentrated hydrochloric acid by the addition of water. When hydrolysed, it yields aminomyristicinic acid, which crystallises from alcohol in long, slender, colourless needles, melting and decomposing at 200° . Solutions of the latter substance also show a blue fluorescence:

0.1190 gave 0.2239 CO_2 and 0.0480 H_2O . $C=51.3$; $H=4.5$.

$C_9H_9O_5N$ requires $C=51.2$; $H=4.3$ per cent.

Ethyl Cyanomyristicinate (Ethyl 2-Cyano-3-methoxy-4:5-methylene-dioxybenzoate), V, p. 267.

Ethyl aminomyristicinate was dissolved in rather more than two molecular proportions of hot sulphuric acid (10 per cent.), and the solution cooled, with vigorous agitation. A solution of sodium nitrite (1 mol.) was slowly added at 0°. After some time the mixture was filtered to remove unchanged amino-ester, and the filtrate added in small portions to a hot solution of cuprous cyanide. The mixture was heated on the boiling-water bath for an hour, then cooled, and extracted with ether. The ethereal extract was washed first with sodium hydroxide, which removed some resinous matter, and then with water. On removing the solvent, the residue soon solidified; it was purified by crystallisation from alcohol, and thus obtained in yellow prisms, melting at 111°:

0.1252 gave 0.2652 CO₂ and 0.0534 H₂O. C=57.8; H=4.7.

C₁₀H₇O₅N requires C=57.8; H=4.4 per cent.

Ethyl cyanomyristicinate is readily soluble in benzene, chloroform, or ether, but only moderately so in cold alcohol. When heated for a short time with alcoholic potassium hydroxide, it is converted into *cyanomyristicinic acid*, which crystallises from alcohol in prismatic needles, melting at 221°.

Cotarnic Acid, VI, p. 267.

In order to prepare cotarnic acid from ethyl cyanomyristicinate, the latter was heated with an excess of alcoholic potassium hydroxide until ammonia ceased to be evolved. After removing the alcohol, the alkaline liquid was acidified with dilute hydrochloric acid, and then extracted with ether. The ethereal solution yielded a crystalline residue, which was recrystallised from benzene containing a little methyl alcohol. It was thus obtained in colourless, square prisms, decomposing at 178° with the formation of an anhydride, which then melted at 160° (0.0990 required 8.25 c.c. N/10-KOH for neutralisation. M.W.=240. C₈H₆O₃(CO₂H)₂ requires M.W.=240).

It is evident that the above substance possesses the composition and properties of cotarnic acid. Its identity was further confirmed by conversion into the methylimide of cotarnic acid. This was prepared by dissolving the cotarnic acid in an excess of methylamine solution, evaporating to dryness, and subjecting the methylamine salt to destructive distillation under diminished pressure (compare Perkin, Robinson, and Thomas, *Trans.*, 1909, **95**, 1984). The distillate solidified at once, and on recrystallisation from alcohol was

obtained in colourless needles. When heated in a capillary tube, the methylimide began to change about 186°, and completely melted at 199° with partial volatilisation. (Found, C=56.5; H=4.1. Calc., C=56.2; H=3.8 per cent.)

For purposes of comparison, a specimen of the methylimide of cotarnic acid was prepared by the oxidation of cotarnine (Freund and Wulff, *Ber.*, 1902, **35**, 1739). This product also began to change at about 186°, and melted completely at 199°, whilst admixture with the synthetic methylimide produced no change in the point of fusion. Freund and Wulff * (*loc. cit.*) attribute to the methylimide of cotarnic acid a melting point of 205—206°, but the present author, as seen above, has not been able to confirm this observation.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

XXXIII.—*The Synthesis of 3- β -Aminoethylindole.*

By ARTHUR JAMES EWINS.

A VERY considerable amount of interest has of late centred round a number of amines which may be considered to belong to a special group in that they are derived from the amino-acids of proteins by the removal of carbon dioxide (loss of the carboxyl group). Such bases are often produced by the action of putrefactive organisms on the amino-acids.

The earliest examples of this class of bases were discovered by Brieger in the ptomaines, putrescine and cadaverine. Their formation by the action of putrefactive organisms on the corresponding amino-acids was first established by Ellinger (*Ber.*, 1899, **32**, 3542). Since then amines derived from almost all the known amino-acids have been obtained either by putrefactive processes or by chemical means. The interest attaching to these bases lies in the fact that certain of the more complex amines are possessed of considerable physiological activity, and have been the subject of several recent communications (Barger and Walpole, *J. Physiol.*, 1909, **38**, 343; Dale and Dixon, *J. Physiol.*, 1909, **39**, 25; Acker-

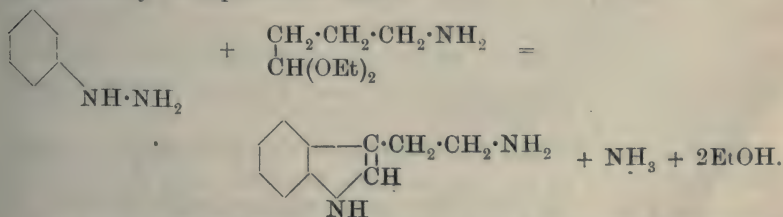
* Since writing the above the author has received a private communication from Dr. M. Freund stating that the melting point previously ascribed to the methylimide of cotarnic acid is incorrect. A specimen of this substance kindly sent by Dr. Freund, to whom the author desires to express his sincere thanks, melted at 199° and was identical with the compound described in this investigation.

mann and Kutscher, *Zeitsch. Biol.*, 1910, **54**, 387; Barger and Dale, *Trans.*, 1910, **97**, 2592; Dale and Laidlaw, *J. Physiol.*, 1910, **41**, 318).

Of the amino-acids known to occur in proteins for which the corresponding amine remained unknown, tryptophan is the most important. This amino-acid was first isolated by Hopkins and Cole (*J. Physiol.*, 1901-1902, **27**, 418), and afterwards synthesised by Ellinger and Flamand (*Ber.*, 1907, **40**, 3029). The amine derived from this amino-acid has now been obtained both synthetically and by the action of putrefactive bacteria on tryptophan itself (Ewins and Laidlaw, *Proc.*, 1910, **26**, 343), and the method of synthesis forms the subject of the present communication. (The action of putrefactive bacteria on tryptophan had previously been studied, but the isolation of the base was achieved only when its synthesis had revealed the properties of the amine.)

It was at first hoped that by heating tryptophan under very greatly diminished pressure, carbon dioxide might be split off, as in the case of tyrosine. This experiment was carried out at Dr. G. Barger's suggestion but the only product that could be isolated from the sublimate was a very small quantity of unchanged tryptophan. The method employed by Windaus and Vogt (*loc. cit.*) in the synthesis of 4- β -aminoethylglyoxaline from β -glyoxaline-4-propionic acid derived from histidine cannot here be employed, owing to the action of nitrous acid on the indole nucleus.

The method ultimately adopted was a modification of Fischer's method of synthesising indole derivatives, in which the phenylhydrazone of the suitable aldehyde is heated with zinc chloride. In this instance, the requisite aldehyde cannot be isolated in the free state on account of the readiness with which condensation takes place with formation of cyclic compounds (Wohl and Schäfer, *Ber.*, 1905, **38**, 4157). It was found, however, that the corresponding acetal (γ -aminobutyrylacetal) could be employed in place of the aldehyde, and that by heating with zinc chloride and phenylhydrazine, condensation was effected, alcohol and ammonia being eliminated, and a good yield of the desired base thus obtained. The reaction may be represented thus:

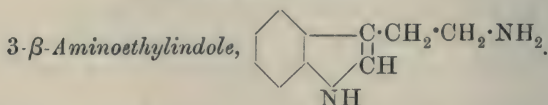


The picrate of the base was found to be identical in all respects,

chemical and physiological, with that of the base obtained by the action of putrefactive bacteria on tryptophan. This fact, the method of formation, and the analytical results leave no doubt as to the constitution of the base. As might be expected, the base gives the glyoxylic (Adamkiewicz) reaction described in detail by Hopkins and Cole (*Proc. Roy. Soc.*, 1901, **68**, 21) as a reaction for tryptophan. With bromine, however, which with tryptophan gives a pink colour, no reaction is obtainable.

As was expected, the base proved to be physiologically active. Dr. P. P. Laidlaw, who is undertaking its physiological examination, and by whom a full account of its action will be communicated elsewhere, has found that among other effects it produces a rapid and marked rise of blood pressure.

EXPERIMENTAL.



Four grams of γ -aminobutyrylacetal (b. p. 104—106°/18 mm.), obtained according to the method employed by Wohl and Schäfer (*Ber.*, 1901, **34**, 1914), were heated to 180° for three hours with 2.6 grams of phenylhydrazine and 3.6 grams of anhydrous zinc chloride in an open vessel. The product was dissolved in dilute acetic acid, the solution extracted with ether, and the zinc removed from the acetic acid solution as sulphide. The filtrate was then concentrated under diminished pressure to about 10 c.c. On cooling, a crystalline precipitate separated, which was collected. The crude hydrochloride thus obtained was dissolved in a small quantity of water, and an excess of an aqueous solution of sodium hydroxide added. An oil separated which, on keeping, crystallised to a mass of fine needles. The base thus obtained was recrystallised from a mixture of alcohol and benzene, and separated in long, colourless needles, melting at 145—146°. Yield, 45 per cent. of the theoretical:

0.1400 gave 0.3862 CO₂ and 0.0960 H₂O. C = 75.2; H = 7.6.

C₁₀H₁₂N₂ requires C = 75.0; H = 7.5 per cent.

3- β -Aminoethylindole is readily soluble in alcohol or acetone, and almost insoluble in water, ether, benzene, or chloroform. The base decomposes on heating under the ordinary pressure, yielding volatile products having an indole-like odour.

The free base (as well as its salts) gives the bluish-violet coloration with glyoxylic acid and concentrated sulphuric acid described by Hopkins and Cole (*loc. cit.*) as a characteristic reaction of tryptophan. The reaction may be obtained with a solution of one part of the base in about 300,000 parts. With bromine, however,

no coloration is obtained, the base differing in this respect from tryptophan, which gives a pink colour.

3- β -Aminoethylindole Hydrochloride, $C_{10}H_{12}N_2 \cdot HCl$.

The crude hydrochloride of 3- β -aminoethylindole, obtained as described above, was recrystallised from 95 per cent. alcohol by careful addition of ether. The salt was thus obtained in colourless, thin prisms, melting at 246° :

0.1444 gave 0.1058 AgCl. $Cl = 18.1$.

$C_{10}H_{12}N_2 \cdot HCl$ requires $Cl = 18.1$ per cent.

The hydrochloride is soluble in about 12 parts by weight of water at 18° , and very soluble in hot water, from which it may be recrystallised.

3- β -Aminoethylindole Picrate, $C_{10}H_{12}N_2 \cdot C_6H_2(NO_2)_3 \cdot OH$.

This salt, the most characteristic of the base, is readily obtained by addition of a cold saturated aqueous solution of picric acid to a solution of the hydrochloride in water. The mixture immediately becomes turbid and orange-red in colour, and dark red crystals, consisting of fern-like aggregates of needles or prisms (very similar in form to that of ammonium chloride), rapidly separate. The picrate is characterised by its general insolubility. It is almost insoluble in water, very sparingly soluble in alcohol, ethyl acetate, chloroform, and most organic solvents except acetone, in which it is readily soluble.

For analysis, the salt was recrystallised from dilute acetone. The pure picrate melted and decomposed at $242-243^\circ$:

0.1286 gave 0.2338 CO_2 and 0.0452 H_2O . $C = 49.6$; $H = 3.9$.

$C_{16}H_{15}O_7N_5$ requires $C = 49.3$; $H = 3.85$ per cent.

3- β -Aminoethylindole picrolonate was prepared by adding rather more than one molecular proportion of picrolonic acid in dilute alcoholic solution to an aqueous solution of the hydrochloride. On concentrating the mixture, a crystalline solid separated, which was readily recrystallised from hot water, and separated in bundles of short, stout, deep chrome-yellow prisms, melting and decomposing at 231° .

The *benzoyl* derivative, obtained by the Schotten-Baumann method, or by heating the base with benzoic anhydride, is not readily obtained crystalline. It may be crystallised by very slow evaporation of the alcoholic solution of the compound, or by very careful addition of light petroleum to its solution in dry ether or ethyl acetate, and is then obtained in stout prisms, melting at $137-138^\circ$.

THE WELLCOMBE PHYSIOLOGICAL RESEARCH LABORATORIES,
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XXXIV.—*The Colour and Constitution of Bromine Solutions.*

By ALFRED FRANCIS JOSEPH and JAMES NADORIS JINENDRADASA.

IF a soluble bromide is added to bromine water, the colour of the solution is greatly diminished, the effect depending to some extent on the amount of bromide added, and it was thought that a quantitative examination of such colour changes might afford additional evidence for the constitution of bromine solutions which has been adduced from the study of their other properties. The experiments of Worley (Trans., 1905, **87**, 1107) confirmed the views of previous workers, that a considerable part of the bromine was in the form of tribromide, and he found values for the dissociation constant in the equation:

$$k(\text{KBr}_3) = (\text{KBr}) \times (\text{Br}_2)$$

varying from 0.03 to 0.07, the variation being probably due to the presence of a portion of the bromine in the form of pentabromide.

The experiments recorded in this paper have led to a similar result, and have been extended to sodium bromide and hydrobromic acid; the presence of the compounds NaBr_3 and HBr_3 is similarly to be inferred, the dissociation constants of these being practically the same as that of the compound KBr_3 .

The method adopted consisted of finding the strengths of bromine and bromine-bromide solutions having the same intensity of colour.

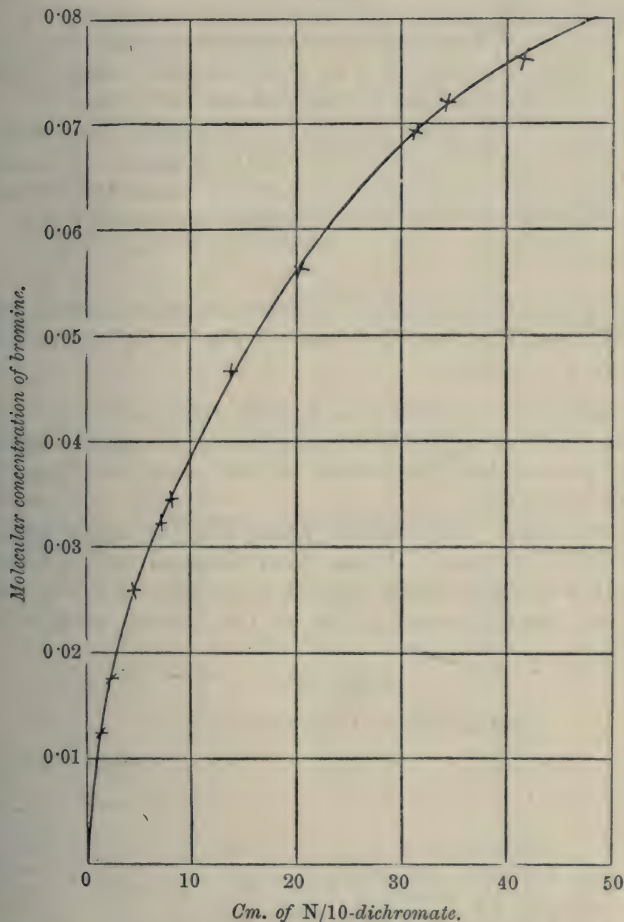
Experiments with the colorimeter on bromine solutions are complicated by rapid loss of bromine from the surface when contained in an open vessel, and consequent lack of homogeneity of the liquid. It is essential that the liquid should be contained in a covered vessel which it completely fills, to enable concordant results to be obtained.

In comparing colours of the solutions, it was thus difficult to use standard bromine solutions the depth of which could be varied at will, and it became necessary to work with a third non-volatile substance, first with bromine water and then with bromine in potassium bromide; in this way, a relation could be obtained between the two latter.

A Duboscq colorimeter was used for the comparisons. In this instrument good diffused daylight reflected from a porcelain plate passes up through two vessels containing the liquids to be compared. A hollow glass cylinder closed at both ends dips into the standard

liquid, and by moving this up or down, the thickness of the layer of liquid between the bottoms of the containing vessel and hollow cylinder can be varied and read off on a scale. The two beams of light, after passing through the liquids, are reflected by prisms so as to illuminate the two halves of the field of an eye-piece.

FIG. 1.



The non-volatile substance used was potassium dichromate, which was chosen on account of the ease with which standard solutions are prepared and kept, and because it can be well matched against bromine.

The standard solutions of dichromate used were $2N$, N , $N/2$, $N/5$, and $N/10$. These are optically equivalent, that is, 4 cm. of a $N/2$ -solution are matched by 1 cm. of a $2N$ -solution, etc.

Bromine and potassium dichromate are not, however, optically equivalent. Their absorption spectra differ, that of the bromine extending further into the red, and ending much less sharply than that of dichromate. Further, if two oblong vessels be filled with bromine and dichromate respectively, so that the colours match when viewed through their long dimensions, the bromine appears far lighter when viewed through their short dimensions.

It has been found that this does not affect the final result, the dichromate being only introduced at an intermediate stage in order to effect comparison between the two bromine solutions.

The first part of the work consisted of comparing the colour of aqueous bromine of various strengths with potassium dichromate solutions, and from the results constructing a calibration curve by plotting strengths of bromine as abscissæ against cm. of $N/10$ -dichromate as ordinates.

Calibration Curve Showing the Relation between the Strength of Bromine contained and the depth in cm. of $N/10$ -Dichromate equivalent in colour.

The bromine was contained in a glass vessel about 2.7 cm. diameter and 1.7 cm. high, the top edge being ground and covered by a clear glass disk. The volume of the vessel was found by weighing to be 9.5 c.c.

The cell was filled with bromine water, and the colour matched with suitable dichromate. It was then dropped into potassium iodide, and the liberated iodine titrated with standard thiosulphate, whereby the molecular concentration of the bromine solution was determined.

TABLE I.

Construction of Calibration Curve.

Standard bi-chromate used.	Colorimeter readings.						Mean.	Colour of di-chromate in cm. $N/10$.	Molecular concentration of bromine water.
$N/10$	1.18,	1.20,	1.20,	1.13,	1.14,	1.18	1.17	1.17*	0.0122
$N/5$	1.16,	1.16,	1.17,	1.13,	1.18,	1.15	1.16	2.32	0.0177
$N/5$	2.25,	2.19,	2.25,	2.18,	2.26,	2.24	2.23	4.46	0.0261
$N/2$	1.47,	1.46,	1.41,	1.36,	1.45,	1.49	1.44	7.20	0.0323
$N/2$	1.60,	1.68,	1.64,	1.69,	1.55,	1.62	1.63	8.18	0.0347
N	1.39,	1.28,	1.39,	1.43,	1.40,	1.46	1.39	13.9	0.0464
N	2.14,	2.01,	2.02,	2.08,	2.01,	2.04	2.05	20.5	0.0556
$2N$	1.58,	1.56,	1.50,	1.67,	1.55,	1.50	1.56	31.2	0.0689
$2N$	1.75,	1.70,	1.67,	1.80,	1.75,	1.65	1.72	34.4	0.0720
$2N$	2.10,	2.11,	2.06,	2.04,	1.99,	2.18	2.09	41.8	0.0758
$2N$	2.78,	2.56,	2.83,	2.64,	2.56,	2.81	2.70	54.0	0.0845

* The mean multiplied by ten times the normality factor gives the colour in cm. of $N/10$ -dichromate.

The last two columns plotted give the calibration curve shown in Fig. 1 (p. 275).

Comparison of the Strengths of Solutions of Bromine in Water and in Aqueous Potassium Bromide, having the same colour.

A solution of bromine in potassium bromide solution of the required strength was placed in the cell and matched against a suitable dichromate solution. By means of the calibration curve, the strength of bromine water having the same colour was read off, and this was taken as the colour of the bromine-bromide solution, the unit of colour being that of aqueous bromine containing 1 gram-molecule per litre. The concentration of the bromine in the solution under examination was determined as before with potassium iodide and standard thiosulphate.

Only the mean of the colorimeter readings is given here, the agreement being of the same order as that shown by the calibration figures. At least six readings were made for each determination.

TABLE II.

Influence of Potassium Bromide on the Colour.

Molecular concentration of potassium bromide.	Standard dichromate used.	Mean colorimeter reading.	Colour expressed in strength of Br ₂ (from the calibration curve).	Bromine concentration (from the titration).
0.1	N/10	1.83	0.015	0.0255
0.1	N/5	1.29	0.018	0.0305
0.1	N/2	2.12	0.040	0.0620
0.1	N	1.51	0.0485	0.0712
0.1	2N	1.94	0.075	0.1071
0.4	N/5	2.58	0.027	0.0665
0.4	N/2	1.18	0.029	0.0708
0.4	N	1.09	0.041	0.0984
0.4	N	1.77	0.053	0.1239
0.4	2N	0.98	0.056	0.1305
0.4	2N	2.26	0.0785	0.1835
1.0	N/5	1.34	0.018	0.0547
1.0	N/2	1.05	0.027	0.0839
1.0	2N	0.45	0.037	0.1062
1.0	2N	1.10	0.0585	0.1811
1.0	N	2.13	0.0575	0.1830
1.0	2N	1.57	0.069	0.2060
1.0	2N	2.10	0.0765	0.2362
1.0	2N	2.38	0.0795	0.2592

The last two columns are plotted in Fig. 2, the colour of bromine water being shown as a straight line with equal ordinates and abscissæ.

A vertical line drawn across the diagram gives the colours of solutions having the same bromine concentration, and the numbers so obtained show the effect of increasing the concentration of the

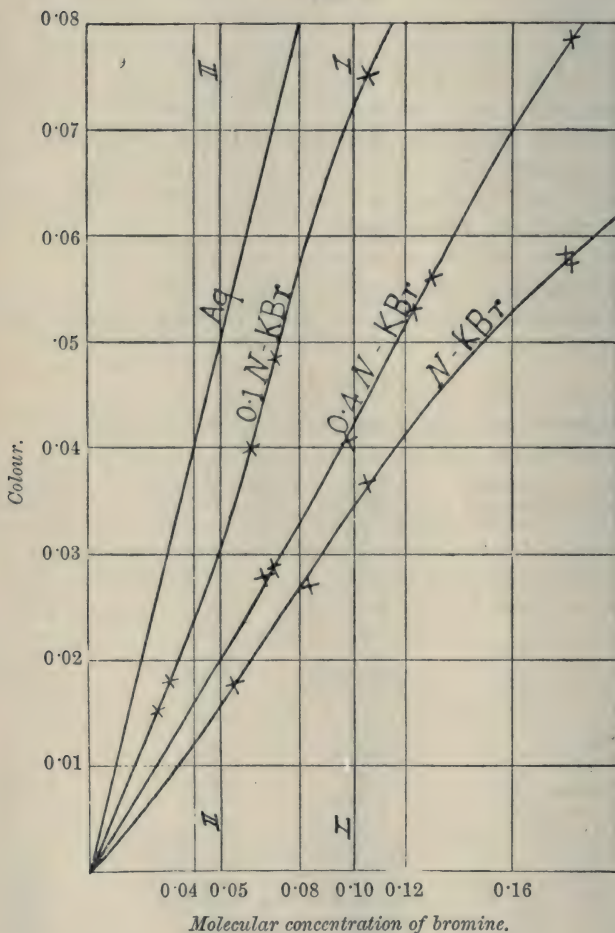
potassium bromide on the colour of a bromine solution of fixed strength.

Thus, at line 1, where concentration of bromine is

0.1, when the conc. of KBr is 0.1, 0.4, 1.0

the colour is 0.07, 0.0415, 0.034,

FIG. 2.



and at line 2, where concentration of bromine is

0.05, when the conc. of KBr is 0.1, 0.4, 1.0

the colour is 0.032, 0.02, 0.016.

These numbers indicate clearly that whilst the addition of a small quantity of bromide causes a very marked falling off in the intensity of the colour, continued addition produces far less effect, and after

the concentration of potassium bromide has reached about 0.8, further addition produces little change.

As a further example, a solution of 0.204 molecular proportion of bromine in *N*-potassium bromide had a colour 0.065, whilst in 2*N*-potassium bromide the colour was 0.062; doubling the concentration of the bromide has thus little effect on the colour.

Colour change in solution may be caused by increase or decrease of electrolytic dissociation or change in constitution (compare Sidgwick and Tizard, *Trans.*, 1908, **93**, 187).

Since Jakowkin (*Ber.*, 1897, **30**, 518) found that bromine water cannot be ionised to any considerable extent, the addition of a soluble bromide could hardly increase its dissociation.

A few experiments were made with the view of determining the effect of the addition of bromine on the conductivity of potassium bromide solutions, and it was found that at 25° the addition to 0.4*N*-potassium bromide of 0.2 gram-molecule of bromine per litre lowers its conductivity about 8 per cent., 0.2 gram-molecule per litre of the non-electrolyte sugar lowering it about 12 per cent. The lowering may be due to viscosity changes, and is in harmony with the view that no great change in ionic concentration is caused by the addition of the bromine.

The colour changes must therefore almost certainly be due to some change of constitution, the simplest of which would be the formation of the compound KBr_3 .*

In the simple treatment that follows, it is assumed that the limit of colour change is reached in normal potassium bromide solution. It is further assumed that potassium tribromide is the only additive compound the presence of which need be considered.

If, then, after this concentration has been reached, further addition of potassium bromide produces no effect, the whole of the bromine must be in the combined state, and the colour of the solution in *N*-potassium bromide (within the limits of bromine concentration here dealt with) is due to potassium tribromide, and not to free bromine.

Consider a solution of bromine in potassium bromide, the total concentration of the dissolved bromine being a . Let its colour be C . Further, let the colour of a solution of potassium tribromide (that is, bromine in *N*-potassium bromide) of molecular concentration a be P . Then, in the solution under discussion, the colour is due partly to free bromine (say, concentration x) and partly to

* The formation of Br_3^- ions would be attended by diminution of conductivity owing to their probably having lower mobility. Bray and Mackay (*J. Amer. Chem. Soc.*, 1910, **32**, 919) have shown the diminution in conductivity brought about by dissolving iodine in aqueous potassium iodide, and caused by the lower mobility of the I_3^- ion.

potassium tribromide ($a-x$). Now, assuming that decrease in colour is proportional to the amount of potassium tribromide formed, then the colour of a solution of a gram-mol Br

when conc. of free Br is O is P

„ „ „ „ x „ C

„ „ „ „ a (that is, Br_2Aq) is a ,

so that proportionally

$$\frac{a}{x} = \frac{a-P}{c-P} \text{ or } x = \frac{a(c-P)}{a-P}.$$

The concentration of the free bromine being thus found, that of the potassium tribromide is $a-x$. This, subtracted from the total potassium bromide concentration, gives the uncombined potassium bromide. From these the dissociation constant in the equation:

$$k(\text{KBr}_3) = \text{Br}_2 \times (\text{KBr})$$

can then be calculated.

The value of k is shown for the experiments of table II. The numbers in the first three columns are taken from table II. Those in the fourth are taken from the N -potassium bromide curve in Fig. 2.

TABLE III.

Dissociation Constant of Potassium Tribromide.

Total concentration, KBr.	Total Br = a .	Colour = C .	Colour of KBr_3 solution of concentration $a = P$.	Free Br = x .	KBr_3 = $a - x$.	Free KBr = total KBr - ($a - x$).	k .
0.1	0.0255	0.015	0.0078	0.0104	0.0151	0.0849	0.058
0.1	0.0305	0.018	0.0095	0.0123	0.0182	0.0818	0.055
0.1	0.0620	0.040	0.0198	0.0297	0.0323	0.0667	0.059
0.1	0.0712	0.0485	0.0226	0.0379	0.0333	0.0667	0.076 (?)
0.1	0.1071	0.075	0.0372	0.0579	0.0492	0.0508	0.060
0.4	0.0665	0.027	0.0212	0.0085	0.0580	0.3420	0.050
0.4	0.0708	0.029	0.0225	0.0095	0.0613	0.3687	0.057
0.4	0.0984	0.041	0.0332	0.0115	0.0869	0.3131	0.041
0.4	0.1239	0.053	0.0431	0.0152	0.1087	0.2913	0.041
0.4	0.1305	0.056	0.0458	0.0157	0.1148	0.2852	0.040
0.4	0.1835	0.0785	0.0628	0.0239	0.1596	0.2404	0.036

In taking the colour of the potassium tribromide solutions from Fig. 2, the smoothed curve has not been used, but each pair of consecutive points has been joined by straight lines. The values of k obtained in this way are of the same order of magnitude and constancy as those obtained by Worley, the variations being from 0.03 to 0.07.

A large number of determinations were made to see whether

sodium and hydrogen bromides behaved in the same way, and from the examples given in the next tables it will be seen that the results are quite similar.

TABLE IV.

Dissociation Constant of Sodium Tribromide.

Concen- tration, NaBr.	Total Br = α .	Colour = C .	Colour of NaBr ₃ solution of concen- tration $\alpha = P$.	Free Br = x .	NaBr ₃ = $\alpha - x$.	Free NaBr = total $\alpha - x$.	k .
0.1	0.0519	0.036	0.020	0.0260	0.0259	0.0741	0.074
0.1	0.0689	0.046	0.0255	0.0327	0.0362	0.0638	0.065
0.1	0.0805	0.055	0.0295	0.0402	0.0403	0.0597	0.060
0.1	0.1110	0.077	0.040	0.0580	0.0530	0.0470	0.052
0.4	0.0427	0.019	0.0165	0.0041	0.0386	0.3614	0.038
0.4	0.0762	0.032	0.028	0.0063	0.0699	0.3301	0.030
0.4	0.0866	0.0368	0.0315	0.0083	0.0783	0.3207	0.034
0.4	0.1214	0.053	0.0425	0.0161	0.1053	0.2947	0.045
0.4	0.1720	0.077	0.060	0.0261	0.1459	0.2541	0.045
1.0	0.0323	0.013	—	—	—	—	—
1.0	0.0647	0.024	—	—	—	—	—
1.0	0.1037	0.0375	—	—	—	—	—
1.0	0.1415	0.049	—	—	—	—	—
1.0	0.1824	0.0635	—	—	—	—	—
1.0	0.2440	0.076	—	—	—	—	—

TABLE V.

Dissociation Constant of Hydrogen Tribromide.

Concen- tration, HBr.	Total Br = α .	Colour = C .	Colour of HBr ₃ solution of concen- tration $\alpha = P$.	Free Br = x .	HBr ₃ = $\alpha - x$.	Free HBr = total HBr - ($\alpha - x$).	k .
0.1	0.060	0.039	0.020	0.0285	0.0315	0.0685	0.062
0.1	0.090	0.062	0.031	0.0473	0.0427	0.0573	0.064
0.4	0.065	0.027	0.022	0.0098	0.0552	0.3448	0.061
0.4	0.133	0.0585	0.046	0.0191	0.1139	0.2861	0.048
1.0	0.042	0.015	—	—	—	—	—
1.0	0.079	0.027	—	—	—	—	—
1.0	0.107	0.037	—	—	—	—	—
1.0	0.149	0.052	—	—	—	—	—
1.0	0.188	0.0635	—	—	—	—	—

If curves exhibiting the relation between bromine concentration and colour are plotted, they are found to be almost coincident with the corresponding ones for potassium bromide, the values for k being likewise practically the same.

Summary.

1. Bromides lighten the colour of aqueous bromine solution, the diminution depending on the amount of bromide added. The

results obtained with sodium, potassium, and hydrogen bromides are similar.

2. After the concentration of the bromide has reached normal, further addition produces little effect on the colour. It is therefore assumed that in such solutions practically the whole of the bromine is in the combined state.

3. In bromide solutions of concentration less than normal, the colour is due partly to free and partly to combined bromine, the amounts of which can be calculated with the aid of the curves.

4. Application of the law of mass-action to the results supports the view that the principal reaction causing the colour change is the formation of a tribromide, the dissociation constant of which is about 0.05.

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XXXV.—*The Condensation of Aromatic Aldehydes with Nitromethane.*

By FREDERIC GEORGE PERCY REMFY.

IN the course of some experiments on the condensation of nitromethane with aromatic aldehydes by means of alcoholic potassium hydroxide, it was found that the facility with which condensation took place was greatly affected by the character as well as the position of substituting groups in the benzene nucleus. An indication that such would be the case was given by the results obtained by previous investigators. Thus Posner (*Ber.*, 1898, **31**, 656), using zinc chloride as condensing agent, was able to prepare *o*-nitrostyrenes from *o*- and *m*-nitrobenzaldehyde, but not from the para-compound or other substituted benzaldehydes even when using different condensing agents. On the other hand, Thiele (*Ber.*, 1899, **32**, 1293), by the use of alcoholic potassium hydroxide, was able to obtain, apparently in each case with equal ease, *o*-*o*-, *o*-*m*-, and *o*-*p*-dinitrostyrene. It was deemed of interest to make an extended study of the condensation products of nitromethane with various substituted benzaldehydes with the view of ascertaining, so far as possible, the conditions which govern this reaction. A large number of aromatic aldehydes were therefore treated with nitromethane in the presence of alcoholic potassium hydroxide under exactly similar conditions. The results obtained, however, do not admit of any generalisation with regard to the condensation of aromatic aldehydes with nitromethane, but have given some

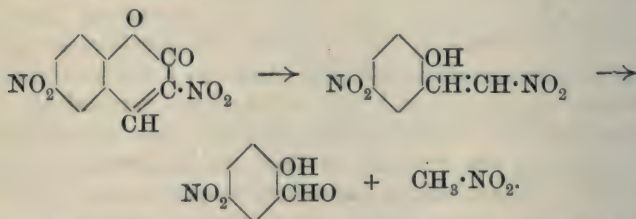
indication of the effect of certain groups in various positions; anomalies have, however, been observed.

Commencing with monosubstituted benzaldehydes, it was found that the hydroxyl groups in the ortho- or meta-position exercised no influence on the course of the reaction, but that a para-hydroxyl group, either alone or in conjunction with other groups (except in one instance), rendered condensation impossible. If, however, the para-hydroxyl group is closed by such means as methylating (Rosenmund, *Ber.*, 1909, **42**, 4780), acetylating, or benzoylating, then condensation readily occurs. A free carboxy-group in the molecule prevents condensation, as is seen in the cases of *m*- and *p*-aldehydophenoxyacetic acids, but the esters of these two acids behave quite differently, and readily form nitrostyrenes. *p*-Chlorobenzaldehyde, on the other hand, readily condenses with nitromethane. Thiële (*loc. cit.*) has already shown that the presence of a single nitro-group in any position in the ring (*o*-, *m*-, or *p*-, with regard to the aldehyde group) has no effect on the condensation, but, as will be proved later, the same cannot be said of the nitro-group when other substituents, which by themselves have no influence on the course of the reaction, are introduced as well. Both 3-nitro-4-methoxybenzaldehyde and 3:5-dinitro-4-methoxybenzaldehyde, where one and two nitro-groups respectively have been introduced into *p*-methoxybenzaldehyde, show a readiness to form nitrostyrenes about equal to that of the parent substance. 3-Nitro-4-hydroxybenzaldehyde, however, having a free *p*-hydroxy-group, follows the hydroxyl rule, and does not condense.

The one apparent exception to this rule is found in 5-aldehydosalicylic acid, which readily combines with nitromethane. This exceptional reaction may be explained by the supposition that in solution a lactone is formed, and hence no free *p*-hydroxy-group is really present. In support of this theory, it was found that if the carboxylic acid was esterified, no condensation took place, the formation of a lactone being then impossible, and the *p*-hydroxy-group being thus free to exercise its obstructive effect. Similarly, 3-aldehydosalicylic acid may be considered to form a lactone, seeing that condensation takes place; on esterification, however, no condensation occurs. This was certainly unexpected, seeing that a free *o*-hydroxy-group alone does not hinder condensation, and all cases in which a carboxylic ester has been the only substituent in the molecule have proved amenable to condensation.

The addition of a nitro-group to either of these aldehydo-acids prevents condensation, presumably by hindering the closing of the lactone ring. When two hydroxy-groups are present in the ortho- and meta-position, the aldehyde acts normally, that is, as if only

one were present at a time, and condensation readily takes place. When, however, one of the hydroxy-groups is in the para-position, no styrene is formed. This was found on trying to condense the carbonate of 3:4-dihydroxybenzaldehyde with nitromethane, potassium hydroxide at once liberating the hydroxy-groups, and a quantitative yield of protocatechualdehyde being obtained. When the hydroxy-groups are bound, however, as in 3:4-methylenedioxybenzaldehyde, condensation readily takes place, as would be expected. While experimenting with nitrosalicylaldehydes, it was found that the position of the nitro-groups was of importance, for whereas 3-nitrosalicylaldehyde undoubtedly formed a nitrostyrene, although in small quantities, the 5-nitro-compound did not. Additional evidence of the fact that 5-nitrosalicylaldehyde does not condense in the usual way with nitromethane is furnished by Clayton (Trans., 1910, **97**, 1390), who obtained nitrostyrenes by the action of alkalis on certain derivatives of coumarin. In the case of 3:6-dinitrocoumarin, however, the reaction proceeded in the following manner:



In order to account for the production of 5-nitrosalicylaldehyde, the intermediate formation of ω -5-dinitro-2-hydroxystyrene must be supposed, but no trace of it could actually be isolated. This evidence cannot, however, be taken as strong proof that 5-nitrosalicylaldehyde will not under any conditions condense with nitromethane to form the desired nitrostyrene, seeing that Clayton treated the different coumarins with boiling aqueous alkali hydroxide or ammonia, whilst in the experiments described in this paper, temperatures below 0° were employed, and even then in some cases only a very small quantity of condensation product was obtained. It may, however, be assumed from Clayton's work that the presence of an alkyl group in any position round the ring has no effect whatever on the course of the reaction with nitromethane. Moreover, it has been found that 1-aldehyde- β -naphthol condenses just as readily as salicylaldehyde.

EXPERIMENTAL.

In all the experiments described in this paper, the method of procedure was practically identical, and, except in the matter of temperature, was similar to the method described by Rosenmund

(*Ber.*, 1909, **42**, 4780), Thiele, however, being the first to make use of alcoholic potassium hydroxide as a condensing agent in this reaction (*Ber.*, 1899, **32**, 1294), whereby he prepared styrenes from *o*-, *m*-, and *p*-nitrobenzaldehyde and terephthalaldehyde. A short account of the process in the first experiment will therefore serve for all.

One molecular quantity of the aldehyde was dissolved in sufficient absolute alcohol to prevent it crystallising out when the temperature of the solution was lowered to about -5° by a freezing mixture. To this was added one and a-quarter molecular quantities of nitromethane. (Where a carboxyl or hydroxyl group is present in the molecule of the particular aldehyde to be condensed with nitromethane, one molecule of potassium hydroxide is added to neutralise it and one to effect the condensation.) Two molecular proportions of 50 per cent. potassium hydroxide, dissolved in about ten volumes of absolute alcohol, after being cooled below 0° , were slowly dropped from a tap funnel into the solution of the aldehyde, which was kept well stirred, and the temperature was not allowed to rise above 0° . As soon as all the alkali had been introduced, the alcoholic solution was diluted with an equal volume of water and rendered just acid by the addition of dilute hydrochloric acid. In many cases the required nitrostyrene crystallised direct from this solution, and was collected, washed with water, and recrystallised. If crystallisation did not take place, the excess of alcohol was removed, and the condensation product, as a rule, quickly separated from the aqueous liquor. Failing this, extraction with ether was resorted to.

For the sake of brevity and clearness, the compounds have been arranged in tabular form (p. 286), no detailed description of each substance being necessary, except in a few cases, owing to the similarity of their properties and methods of preparation. Except where mentioned otherwise, the colour of these compounds is of varying shades of yellow. All those aldehydes which were found to condense with nitromethane to form nitrostyrenes have been placed in table I, whilst those which did not are to be found in table II

β -3: 5-Trinitro- α -hydroxy-4-methoxy- α -phenylethane,
 $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NO}_2.$

This substance was obtained when attempting to prepare ω -3: 5-trinitro-4-methoxystyrene. The results of the analyses show that water had not split off to form the expected styrene:

0.1310 gave 0.1840 CO_2 and 0.0371 H_2O . $\text{C} = 38.3$; $\text{H} = 3.17$.

0.1524 „ 0.2138 CO_2 „ 0.0447 H_2O . $\text{C} = 38.3$; $\text{H} = 3.3$.

TABLE I.

Compound.	Formula.	Crystalline form.	M. p.	Analysis.	
				Found, per cent.	Theory, per cent.
ω -Nitro- <i>o</i> -hydroxystyrene	$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$	Prismatic needles	133—134°	N = 8.7	N = 8.5
ω -Nitro- <i>m</i> -hydroxystyrene	$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$	" "	132—133°	N = 8.6	N = 8.5
ω -Nitro- <i>p</i> -hydroxystyrene*	$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$	Plates	165°	N = 8.6	N = 8.5
ω -Nitro- <i>p</i> -acetoxystyrene	$\text{CH}_3\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$	Needles	158—159°	N = 7.1	N = 6.8
ω -Nitro- <i>p</i> -benzoyloxystyrene	$\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$	Silky needles	156°	N = 5.3	N = 5.2
Ethyl ω -nitrostyryl- <i>p</i> -oxyacetate	$\text{NO}_2\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$	Needles	89°	N = 5.6	N = 5.6
<i>p</i> -Chloro- ω -nitrostyrene	$\text{NO}_2\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$	Nodular aggregates	147—148°	N = 5.8	N = 5.6
Ethyl ω -nitrostyryl- <i>m</i> -oxyacetate	$\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}:\text{CH}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$	Needles	111—112°	N = 7.4	N = 7.6
ω -3-Dinitro-2-hydroxystyrene	$\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$	"	174—175°	N = 13.9	N = 13.3
ω -3-Dinitro-4-methoxystyrene	$\text{OMe}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$	"	165—166°	N = 12.7	N = 12.5
Ethyl 3-aldehydosalicylate	$\text{CHO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Et}$	Colourless needles	66—67°	{ C = 61.5 H = 5.2	{ C = 61.8 H = 5.1
Phenylhydrazone of 3-aldehydosalicylic acid	$\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2$	Amber prisms	188°	N = 11.0	N = 10.9
ω -Nitro-2-hydroxy-3-carboxystyrene	$\text{OH}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$	Needles	231°	N = 6.5	N = 6.7
5-Nitro-3-aldehydosalicylic acid †	$\text{C}_8\text{H}_5\text{O}_6\text{N}$	Colourless needles	195—196°	N = 6.9	N = 6.6
Ethyl 5-aldehydosalicylate	$\text{CHO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Et}$	Colourless prisms	69°	{ C = 61.8 H = 5.3	{ C = 61.8 H = 5.1
Phenylhydrazone of ethyl 5-aldehydosalicylate	$\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}_2$	Prisms	135—136°	—	—
Phenylhydrazone of 5-aldehydosalicylic acid	$\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2$	Prismatic needles	219°	N = 11.1	N = 10.9
Ethyl 3-nitro-5-aldehydosalicylate	$\text{C}_{10}\text{H}_9\text{O}_6\text{N}$	Colourless needles	79—80°	N = 6.0	N = 5.8
1- ω -Nitrovinyl- β -naphthol	$\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}:\text{CH}\cdot\text{NO}_2 + 2\text{H}_2\text{O}$	Red needles	187—188°	N = 5.5	N = 5.6

* Obtained by saponification of the acetyl derivative in weak alcoholic hydrochloric acid solution.

† Prepared in the same way as 3-nitro-5-aldehydosalicylic acid.

0.1278 gave 15.7 c.c. N_2 at 24° and 770 mm. $N=14.4$.

$C_9H_9O_8N_3$ requires $C=37.6$; $H=3.14$; $N=14.6$ per cent.

($C_9H_7O_7N_3$ „ $C=40.1$; $H=2.6$; $N=15.6$ „)

Moreover, this substance is readily soluble in dilute alkali hydroxides, whereas nitrostyrenes are almost insoluble.

3-Nitro-5-aldehydosalicylic Acid.

5-Aldehydosalicylic acid is dropped in small portions into a mixture of a little more than the theoretical quantity of nitric acid ($D\ 1.42$) and twelve times its weight of concentrated sulphuric acid kept at a temperature of between -5° and -10° by a freezing mixture. After remaining at the ordinary temperature for two hours, the solution is poured on to ice, the resulting solid collected, washed with a little ice-water, and crystallised from hot water. Fine yellow needles are obtained, which give off water of crystallisation rapidly at 110° , and melt at 177° . For analysis, the substance was dried at 100° :

0.1543 gave 9.4 c.c. N_2 at 21° and 771 mm. $N=7.2$.

$C_8H_5O_6N$ requires $N=6.6$ per cent.

0.5866 lost 0.0450 H_2O at 110° . $H_2O=7.67$.

$C_8H_5O_6N, H_2O$ requires $H_2O=7.42$ per cent.

β -Nitro- α -2: 5-trihydroxyphenylethane.

As nothing crystalline separated from the reaction mixture, this was extracted with ether, the ether dried and evaporated, when a dark oil was left. After long keeping in an evacuated desiccator, the oil gradually crystallised. The crystals were freed from adherent oil by pressing on porous plate, and dissolved in dilute alcohol, from which large, prismatic needles of a ruby colour crystallised out. On drying in the air, the colour changed to a brick red, and the crystals then melted at 182° . For analysis, they were dried, first at 100° , then at 110° :

0.1272 gave 7.7 c.c. N_2 at 22° and 757 mm. $N=7.0$.

$C_8H_9O_5N$ requires $N=7.0$ per cent.

The styrene of the above contains 7.7 per cent. of nitrogen, and from the result of the analysis it was evident that the above alcohol had been obtained instead.

Condensation Product of Nitromethane and 5-Nitrosalicylaldehyde.

After having removed some of the alcohol which served as solvent during the condensation, the first crop of crystals proved to be unchanged 5-nitrosalicylaldehyde. Subsequent crops were found to be mixtures, and, to effect a separation, they were each

in turn dissolved in ether, the solution shaken with a concentrated solution of sodium hydrogen sulphite to remove unchanged aldehyde, then once with water, and afterwards dried over calcium chloride. On evaporating off the ether, an almost colourless substance remained. This was crystallised from glacial acetic acid, from which were obtained pale straw-coloured, needle-shaped crystals, melting at $237\text{--}238^\circ$. The yield was very small. After drying in an evacuated desiccator, the substance was analysed:

0.1320 gave 17.2 c.c. N_2 at 21° and 770 mm. $\text{N} = 15.4$.

0.1234 „ 16.2 c.c. N_2 „ 22° „ 765 mm. $\text{N} = 15.4$.

0.1268 „ 0.2154 CO_2 and 0.0382 H_2O . $\text{C} = 46.3$; $\text{H} = 3.43$.

$\text{C}_7\text{H}_6\text{O}_4\text{N}_2$ requires $\text{C} = 46.1$; $\text{H} = 3.2$; $\text{N} = 15.4$ per cent.

($\text{C}_8\text{H}_6\text{O}_5\text{N}_2$ „ $\text{C} = 45.7$; $\text{H} = 2.9$; $\text{N} = 13.3$ „)

The results of the analyses prove that the substance obtained was not the expected ω -5-dinitro-2-hydroxystyrene, but a compound having the empirical formula $\text{C}_7\text{H}_6\text{O}_4\text{N}_2$.

TABLE II.

Aldehydes which will not Condense with Nitromethane.

p-Hydroxybenzaldehyde.
p-Aldehydophenoxyacetic acid.
m-Aldehydophenoxyacetic acid.
 3-Nitro-4-hydroxybenzaldehyde.
 Ethyl 3-aldehydosalicylate.

5-Nitro-3-aldehydosalicylic acid.
 Ethyl 5-aldehydosalicylate.
 3-Nitro-5-aldehydosalicylic acid.
 Ethyl 3-nitro-5-aldehydosalicylate.
 Protocatechualdehyde.

THE WELLCOME CHEMICAL WORKS,
 DARTFORD, KENT.

XXXVI.—*The Interaction of Alloxan and Glycine.*

By WILLIAM HOLDSWORTH HURTLEY and WILLIAM ORD WOOTTON.

STRECKER (*Annalen*, 1862, **123**, 363) was the first to examine the action of alloxan on amino-acids. He found that on warming a solution of alloxan with a solution of leucine, isovaleraldehyde and carbon dioxide were produced, and that alanine, when treated in the same way, gave acetaldehyde and carbon dioxide, whilst glycine gave no aldehyde,* but did give carbon dioxide; in all three cases the liquid assumed the colour of murexide. No quantities are given in Strecker's paper, and he identified his products by qualitative tests only.

Piloty and Finkh (*Annalen*, 1904, **333**, 22), in their paper on

* Formaldehyde was first obtained by Hofmann in 1867.

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FIG. 1.

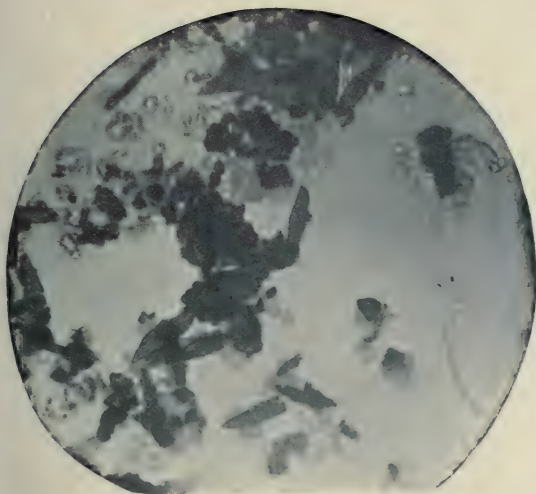
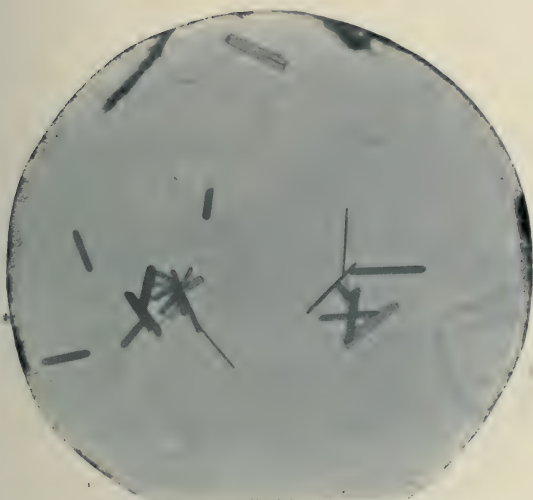


FIG. 2.



Figs. 2 to 7 show the several stages of the reaction as it occurs in moderately dilute solution.

FIG. 3.

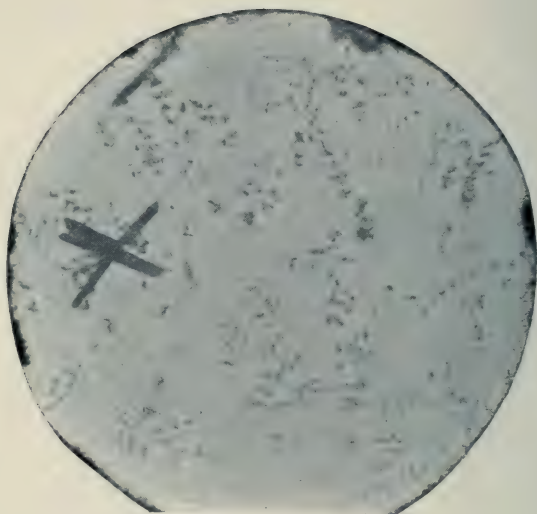


FIG. 4.

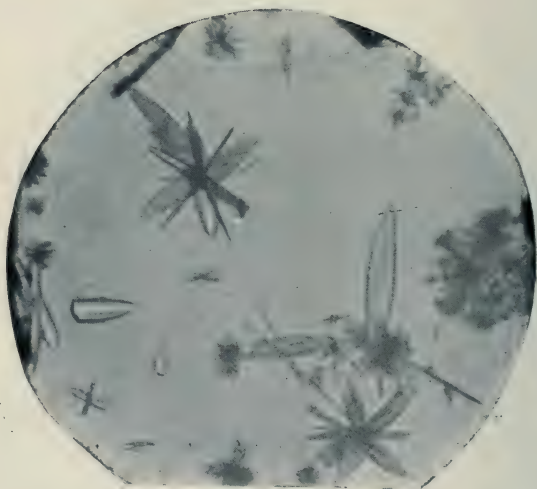


FIG. 5.

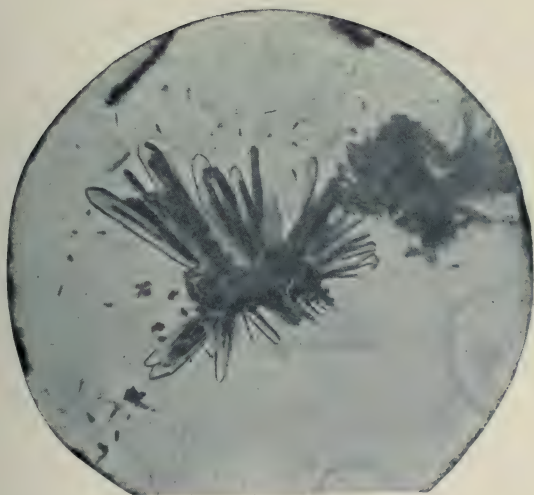


FIG. 6.



FIG. 7.

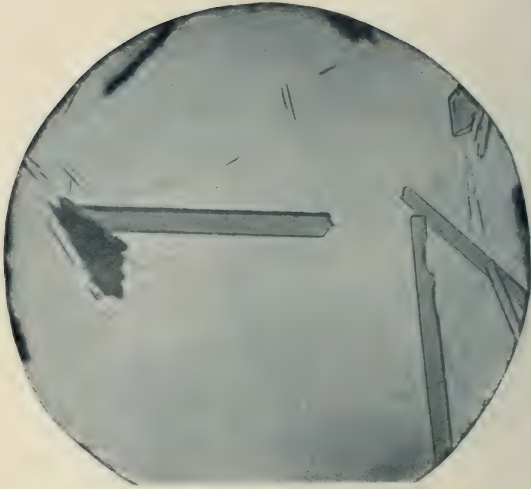
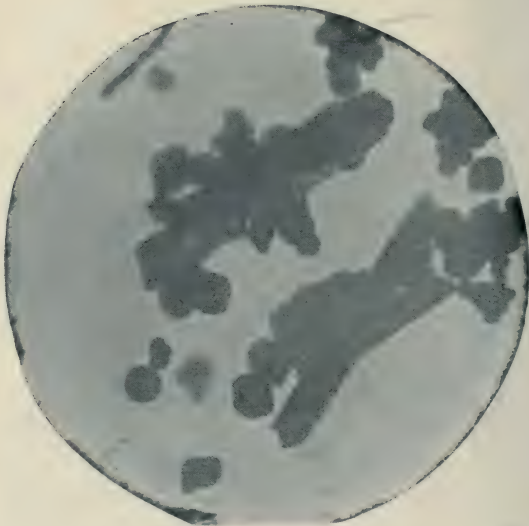
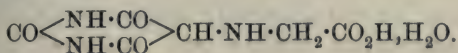


FIG. 8.



the constitution of murexide, describe the interaction of alloxan and glycine when concentrated solutions are mixed at 80°. In these circumstances, the colour of murexide is produced, carbon dioxide is evolved, and, on rapidly cooling, a crystalline product is obtained which has the colour of murexide; this product they describe as glycine purpurate. When, instead of cooling the mixture, it was heated until the colour of the murexide had disappeared, an insoluble, amorphous substance was deposited, and the mother liquor yielded a yellow, crystalline solid, which they describe as uramiloacetic acid:



Piloty and Finkh make no reference to the production of formaldehyde.

The apparently abnormal behaviour of glycine towards alloxan led us to repeat the earlier experiments. In the first place, we confirmed the production of *isovaleraldehyde* from leucine and of acetaldehyde from alanine by preparing the *p*-nitrophenylhydrazones of these aldehydes; we also tried the action of alloxan on α -aminobutyric acid, and were able to show that propaldehyde was produced, which we confirmed by an analysis of the *p*-nitrophenylhydrazone.

When molecular proportions of alloxan and glycine were heated in concentrated solution, no formaldehyde was produced, but we obtained the amorphous substance and the uramiloacetic acid of Piloty and Finkh. When solutions of glycine and alloxan were heated under the exact conditions stated by Piloty and Finkh, we obtained the product they describe as glycine purpurate, also the amorphous substance, and the compound they describe as uramiloacetic acid. Under these conditions, no formaldehyde appears to be liberated. Our analytical results for the glycine purpurate approximate to those of Piloty and Finkh:

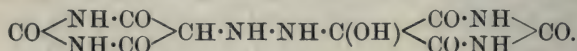
P. and F.	H. and W.
N = 23·89 (dried at 115°)	24·17 (air-dried).
N = 24·46 " "	22·47 (dried at 115°).

On examining the substance under a high power of the microscope, however, it appeared to be far from homogeneous. Fig. 1 shows a typical preparation. It will be seen to contain (a) torpedo-shaped crystals, brown by transmitted and green by reflected light; (b) pink, rectangular crystals, showing light crosses; (c) red, amorphous matter. We prepared the substance six times, always with the like result, and we cannot believe that Piloty and Finkh's glycine purpurate is a definite substance.

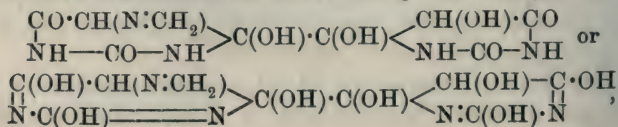
When molecular proportions of alloxan and glycine in dilute solution are distilled, formaldehyde is easily recognised in the

distillate, the yield being about 7.5 per cent. of the theoretical. This low yield of formaldehyde is accounted for below. Under these conditions, Piloty and Finkh's amorphous substance is not obtained. The liquid, which becomes purple soon after mixing, loses its purple colour and turns yellow, crystals of a substance closely related to uramil (the torpedo-shaped crystals referred to above) being deposited. The filtrate from these deposits crystals apparently identical with Piloty and Finkh's uramiloacetic acid. If the acid mother liquor from the product is evaporated, a red, gummy substance is obtained which does not contain oxalic acid, but if the liquor is neutralised with ammonia and then evaporated, crystals of ammonium oxalate are deposited in considerable quantity.

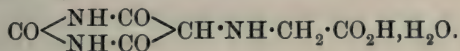
The reaction between these substances evidently occurs at moderate dilutions in several distinct stages. To a certain extent the course of the reaction can be followed by removing drops of the solution at intervals and allowing them to crystallise on a microscope slide. Under these conditions the first substance to appear is murexide, which separates in typical, prismatic crystals (Fig. 2). This is formed even at the ordinary temperature, and its presence is sufficient to account for the purple colour rapidly assumed by the mixed solutions. On warming, the colour of murexide rapidly vanishes, with evolution of carbon dioxide, but at 20° it persists for some time, and in both cases crystals of another substance, distinct from murexide, make their appearance. These are shown in Figs. 3 and 4. This compound is closely allied to uramil, and is readily converted into this substance by repeatedly dissolving it in aqueous sodium hydroxide and precipitating it by hydrochloric acid. On analysis, it gives figures agreeing well with the formula:



On continuing to heat the liquid, it turns yellow, and, on boiling, formaldehyde is evolved. At this stage another substance is produced, namely, the uramiloacetic acid of Piloty and Finkh (Figs. 5, 6, and 7). The results of our analyses of this well-defined compound agree with those of Piloty and Finkh, but we arrive at the formula $\text{C}_9\text{H}_{11}\text{O}_7\text{N}_5$, whereas Piloty and Finkh assign to it the formula $\text{C}_6\text{H}_9\text{O}_6\text{N}_3$. We believe it to be 2:4:6:2':4':5':6'-hepta-hydroxy-5-methyleneamino-4:5:4':5'-tetrahydro-4:4'-dipyrimidyl. (It is referred to hereafter as the reducing substance.)

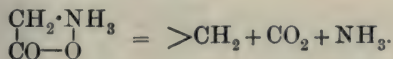


Piloty and Finkh give it the constitution:



Our constitutional formula is based on the following reactions of the substance: (1) When hydrolysed by boiling with water, dilute sulphuric acid or sodium hydroxide, it gives formaldehyde. (2) It has powerful reducing properties; thus, on adding a solution to a dilute solution of silver nitrate or to a dilute solution of gold chloride, it gives in each case a colloidal solution of the metal. (3) Ammonia converts it into an exceedingly insoluble amide. (4) When treated with moderately dilute nitric acid, it gives alloxan and evolves formaldehyde. (5) It is a distinctly acidic substance.

The course of the reaction appears to be as follows: The glycine loses ammonia and carbon dioxide:



whilst the methylene group thus liberated reduces a part of the alloxan to dialuric acid, and is itself converted for the most part into formaldehyde. The unchanged alloxan and the dialuric acid form alloxantin, which, with the ammonia, forms murexide. Direct proof that the liquid contains alloxantin has been obtained. In the acid solution the murexide is transformed into the substance we have described as being closely related to uramil, and this product, or the uramil derived from it, condenses with dialuric acid and formaldehyde to give the reducing substance.

The final gummy product of the reaction has not yet been fully investigated, but from the fact that it readily gives a large yield of ammonium oxalate, it is clearly a product or mixture of products resulting from the opening of the pyrimidine ring.

We have shown that dimethylalloxan also oxidises an α -amino-acid to the next lower aldehyde, and yields tetramethylmurexide. From this it appears certain that in the oxidation of an amino-acid by alloxan, the imino-groups of the latter are not involved.

In addition to the amino-acids mentioned before, we have tried the action of alloxan on tyrosine, tryptophan, cystine, and on glucosamine; all these give a strong murexide colour, and in the case of tyrosine a flowery odour is produced. That alloxan deeply colours the skin has long been known; this action is mentioned by Liebig and Wöhler; we have tried its action on peptone (Witte's), gelatin, and casein. It gives a feeble murexide colour on warming with the first two, but no colour with the third. These results seem to show that alloxan might be of some service in the classification of the proteins. As another matter of biochemical interest we may recall an observation of Liebig to the effect that he found

free alloxan in the jelly-like mucus obtained from a case of intestinal catarrh. The ease with which considerable quantities of ammonium oxalate are formed by the interaction of alloxan and glycine is also of interest when it is remembered that there is some difficulty in accounting for the endogenous oxalates of the urine. Lastly, if the interaction of alloxan and glucosamine follows the normal course, a pentose should be formed from the glucosamine.

The reaction promises to be one of considerable biochemical interest, and is being further studied from this point of view. One of the products described in this paper is being examined as to its physiological action.

EXPERIMENTAL.

Action of Alloxan on α -Aminobutyric Acid.

Twenty-four grams of alloxan dissolved in 50 c.c. of warm water were added to a solution of 10 grams of α -aminobutyric acid in 25 c.c. of warm water. The solution almost immediately became purple-red, and, on heating, a brisk evolution of carbon dioxide occurred, and crystals of murexide separated. On distillation the liquid became dull red, and a micro-crystalline deposit formed, whilst an odour of propaldehyde became perceptible. The distillate reduced ammoniacal silver nitrate, gave a resin with sodium hydroxide, and on treatment with *p*-nitrophenylhydrazine gave a yellow, crystalline hydrazone, melting at 120–121°. (Found, N=22.00. Calc., N=21.76 per cent.)

The yield of aldehyde in this reaction is illustrated by the following figures: 2.2 grams of alloxan and 1.0 gram of α -aminobutyric acid gave 0.67 gram of the *p*-nitrophenylhydrazone; theory requires 1.87 grams. Yield, 35.8 per cent. By using twice the above quantity of alloxan, the yield of hydrazone was raised to 52.4 per cent.

Action of Alloxan on Glycine.

A. *In Concentrated Solutions.*—2.9 Grams of alloxan (1 mol.) and 1 gram of glycine (1 mol.) in 20 c.c. of water rapidly gave a deep purple liquid, and deposited a purple solid. The liquid, after boiling for twenty minutes, gave 0.6 gram of a brick-red solid. The filtrate from this was brownish-yellow, and slowly deposited 0.5 gram of orange crystals. The mother liquor from these, when treated with alcohol, gave a yellow, amorphous precipitate (0.55 gram), and the mother liquor from this precipitate turned red when allowed to remain in the air, and on evaporation deposited a brownish-red, amorphous substance, which was not examined. The brick-red solid was mostly uramil, but contained a yellow substance

sparingly soluble in alkalis, which, on oxidation with bromine water and sodium hydroxide, gave an intense blue fluorescence recalling that observed by Hartley (Trans., 1905, **87**, 1791) in the preparation of murexide from alloxantin by the action of ammonia on it. The orange crystals were identical with a product which is fully described later. The yellow, amorphous substance evolved ammonia freely when boiled with sodium hydroxide; it does not appear to contain the alloxan ring.

B. In Dilute Solution.—A solution of 3.5 grams of glycine and one of 10 grams of alloxan (molecular proportions) were made up to 500 c.c. It gradually became deep purple on heating, and after ten minutes very small, silky crystals separated in great number. These crystals were torpedo-shaped, and with them was a small quantity of minute, needle-shaped crystals; the weight of this product was 1 gram. The filtrate, when evaporated to a smaller bulk on the water-bath, deposited 1.5 grams of yellow crystals. On further concentration, a red, gummy substance remained permeated with yellow crystals. When this gummy substance was allowed to remain in the air or in a vacuum desiccator, it swelled up, owing to a very slow and continuous disengagement of a gas; it was strongly acid, but contained no oxalic acid. On boiling with ammonia, however, it yielded ammonium oxalate. On treatment with nitric acid, it gave, amongst other products, crystals closely resembling those of carbamide nitrate. On boiling with sodium hydroxide, ammonia was evolved.

When this experiment was repeated exactly as above, except that after removal of the yellow crystals 45 c.c. of strong ammonia were added, a white precipitate of minute, felted needles (0.25 gram) was obtained, identical with the amide obtained from the yellow crystals which is referred to later. The filtrate from these, on evaporation, deposited 4.95 grams of ammonium oxalate in colourless, shining needles. (Found, N=17.92. Calc., N=17.50 per cent.)

Besides the substance referred to above, carbon dioxide and formaldehyde were given off when the solution was boiled. The former was estimated by making an experiment on 0.387 gram of glycine, working as above, and it gave 0.236 CO₂, or 96.7 per cent. of the theoretical yield from the glycine; the latter was estimated by making an experiment on 0.511 gram of glycine, working as above, when 0.015 gram of formaldehyde was obtained, or 7.5 per cent. of the theoretical yield from the glycine. The remainder of the formaldehyde split off from the glycine is used up (a) in reducing alloxan, (b) in the production of the reducing substance.

As we have already pointed out, when glycine and alloxan are

allowed to react in hot concentrated solutions, the precipitate obtained, namely, Piloty and Finkh's glycine purpurate, is not a homogeneous substance. When the reaction is performed in dilute solution, the murexide remains in solution, and rapidly undergoes further change. It was isolated as follows: 10 c.c. of a 10 per cent. glycine solution (1 mol.) were mixed with 12.4 c.c. of ammonia (1 mol.), and 20 c.c. of alloxan solution (2 mols.) were added. The mixture immediately became dark purple, and deposited red crystals with a green reflex (0.85 gram). The dried product was seen to consist of murexide-like prisms mixed with about an equal amount of a red powder; a drop of the liquid allowed to crystallise under the microscope deposited typical murexide crystals and spherical aggregates of exceedingly minute crystals (Fig. 8). These two products were separated by sieving through copper gauze of 100 mesh, and analysed:

0.0969 (prisms) gave $N^* = 29.47$.

0.1993 (spheres) gave $N = 29.51$.

$C_8H_8O_6N_6$ requires $N = 29.58$ per cent.

On repeating the last experiment, substituting an equivalent amount of sodium hydroxide for the ammonia, a deep purple liquid was obtained, which deposited a dull red precipitate, consisting of sodium hydrogen purpurate in the form of minute needles. (Found, $N = 25.06$; $Na = 7.98$. Calc., $N = 24.22$; $Na = 7.96$ per cent.)

The substance which immediately succeeds the murexide in the interaction of alloxan and glycine is best obtained by allowing the two substances to react in molecular proportions at the ordinary temperature in dilute solution. Thus, from 5 grams of alloxan, 1.8 grams of glycine, and 250 c.c. of water, a pale pink precipitate of silky, torpedo-shaped crystals appears after an hour:

0.2250 gave 0.2616 CO_2 and 0.0534 H_2O . $C = 32.56$; $H = 2.64$; $N = 27.66$.

$C_8H_8O_7N_6$ requires $C = 32.00$; $H = 2.67$; $N = 28.00$ per cent.

Uramil, $C_4H_5O_3N_3$ requires $C = 33.57$; $H = 3.5$; $N = 29.37$ per cent.

By dissolving in aqueous sodium hydroxide and reprecipitating by hydrochloric acid half a dozen times, this substance gave pure uramil. It is always formed when alloxan acts on glycine, and has always the same curious crystalline form. We think it is probably a definite substance of the above formula. The specimen of uramil obtained from it was analysed. (Found, $C = 33.37$; $H = 3.45$; $N = 29.20$. Calc., $C = 33.57$; $H = 3.5$; $N = 29.37$ per cent.)

The yellow crystals of the reducing substance, which we regard

* Owing to the difficulty of obtaining the nitrogen free from nitric oxide in the ordinary method of combustion, the nitrogen was determined in all cases by Kjeldahl's method.

as the most important product of the reaction, are best obtained as follows: 10 grams of alloxan were dissolved in water and the solution made up to 500 c.c., 1.75 grams of glycine were added, and the whole heated to boiling during fifteen minutes, and then boiled briskly for half an hour. After twelve hours, 0.85 gram of crystals was collected. By concentrating the filtrate on the water-bath, successive crops of 0.4, 1.5, and 0.65 gram of the crystals (total, 3.4 grams) were obtained. The whole yield was crystallised from hot water, taking care to avoid prolonged boiling, which brings about hydrolysis. If in this preparation the volume is made up to 300 c.c. only, the crystals of reducing substance are mixed with the torpedo-shaped crystals described above, and the yield is diminished.

2:4:6:2':4':5':6'-*Heptahydroxy-5-methyleneamino-4:5:4':5'-tetrahydro-4:4'-dipyrimidyl* forms very pale yellow prisms with pointed ends, as shown in Fig. 7. It has no definite melting point, but becomes dark purple at 165°; at 250° it sinters, forming a white sublimate, and there is no melting below 300°. It is sparingly soluble in the usual organic solvents, but dissolves readily in warm water:

0.1829 gave 0.2228 CO₂ and 0.0645 H₂O. C=33.20; H=3.91.

0.1803 „ 0.2207 CO₂ „ 0.0610 H₂O. C=33.38; H=3.79.

0.0652, by Kjeldahl's method, gave N=22.17.

0.2262, „ „ „ „ N=21.79.

C₉H₁₁O₇N₅·H₂O requires C=33.85; H=4.07; N=21.94 per cent.

Piloty and Finkh found for this substance C=33.03; H=3.95; N=21.02. Their formula, C₆H₉O₆N₃ requires C=32.88; H=4.11; N=19.18 per cent. A solution of the compound in water gives with hydrochloric acid a nearly white, crystalline precipitate; the crystals have the same form, and show all the reactions of the original substance, and contain the same amount of nitrogen—an analysis gave 22.29 per cent. On boiling with water or with dilute sulphuric acid, formaldehyde is evolved; an estimation of the aldehyde obtained in each case gave 50 per cent. of that required by the formula assigned to the compound. The substance is readily soluble in sodium hydroxide, and on boiling the solution formaldehyde and ammonia are evolved; this can only be the case if one or both of the rings are opened. Piloty and Finkh's observation that alloxan is produced when the substance is treated with dilute nitric acid was confirmed, but it was also found that much formaldehyde is obtained on warming. If the nitric acid is more concentrated, a beautiful cherry-red liquid is produced. The most remarkable property of the substance is its strong reducing action; thus it reduces Fehling's solution in the cold; it forms colloidal

silver slowly from a neutral solution of silver nitrate at the ordinary temperature; a dilute solution of gold chloride quickly yields a colloidal gold solution, which is brownish-red by reflected and blue by transmitted light. Mercuric chloride is reduced to mercurous chloride also in the cold. It is readily oxidised by potassium permanganate, and yields well-defined products when treated with bromine water and with a solution of iodine in potassium iodide; these substances are at present under investigation.

The aqueous solution, when treated with ammonia and boiled, gave a silky, white precipitate, the liquid turning pink. The precipitate consisted of very minute needles, and it appears to be an *amide* of the reducing substance:

0.1193 gave 0.1554 CO_2 and 0.0470 H_2O . $\text{C} = 36.12$; $\text{H} = 4.38$.

0.0633 „ $\text{N} = 28.75$.

$\text{C}_9\text{H}_{12}\text{O}_6\text{N}_6$ requires $\text{C} = 36.0$; $\text{H} = 4.0$; $\text{N} = 28.0$ per cent.

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XXXVII.—*Different Methods of Applying the Grignard Reagents.*

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IN all those very numerous reactions in which the magnesium alkyl or aryl compounds, discovered by Grignard, are employed for synthetical purposes, the preparation of an ethereal solution of the reagent seems to be generally regarded as a necessary preliminary operation. In most cases this is a very easy task, but the quantity of pure ether required is considerable, and, particularly in the case of some of the aryl halides, the secondary formation of hydrocarbons not only causes loss of material, but often also very great inconvenience in the isolation of the compound which is afterwards prepared.

In synthesising some of the alkyl derivatives of silicon recently described, these disadvantages were overcome entirely, or to a very great extent, by omitting the preliminary preparation of the magnesium compounds. Benzylethylsilicon dichloride, for example, was obtained by gradually adding benzyl chloride to ethylsilicon trichloride in the presence of magnesium and ether (Luff and Kipping, *Trans.*, 1908, **93**, 2006), and the mono-, di-, and tri-benzyl derivatives of silicon tetrachloride were prepared in a similar

manner from benzyl chloride, magnesium, and an ethereal solution of the silicon compound (Martin and Kipping, *Trans.*, 1909, **95**, 306).

In order to ascertain whether this modification of the usual method could be advantageously applied in other cases, a few experiments have been made on the preparation of carbinols from aldehydes, ketones, and esters (Grignard, *Compt. rend.*, 1900, **130**, 1322). The results have shown that in these reactions, also, the preliminary preparation of the magnesium compound is unnecessary, and that a good yield of the desired product is obtained by gradually adding a mixture of the alkyl or aryl halogen compound with the aldehyde, ketone, or ester, to the theoretical quantity of magnesium, which is covered with a little ether. The only instance in which this modified method was found to fail was in the case of acetone; that the process is capable of very general application is shown by the fact that it may serve in the synthesis of compounds, not only of carbon and of silicon, but also of tin.

A direct comparison of the yields obtained by the two methods in a given preparation has not been instituted (except in the case of some silicon compounds, *loc. cit.*), and it may be that sometimes the one, sometimes the other, procedure will give the better results, according to the nature of the interacting substances. It seems, however, that unless such a comparison has been made in a particular case, there is no reason for abandoning the method originally employed by Barbier (*Compt. rend.*, 1899, **128**, 110) in favour of that which is now so generally or universally adopted. In some appropriate instances, in fact, the desired substance may be prepared with the aid of magnesium and the halogen derivative, even when the corresponding Grignard compound cannot be obtained; thus, as Jaworsky has recently shown (*Ber.*, 1909, **42**, 435), many unsaturated alcohols may be prepared by treating ketones with magnesium and allyl bromide or iodide in presence of ether, although magnesium allyl halides of the usual type are unknown.

It need hardly be added that no claim is here made for the discovery of the method which has been studied, but it is hoped that the publication of this note will save time and trouble to many who are working with the Grignard reagents.

EXPERIMENTAL.

In preparing the carbinols by the modified method, the formation of a very small quantity of the Grignard compound was first started in the flask containing the magnesium and anhydrous ether; a mixture consisting of the aldehyde, ketone, or ester with the halogen compound, and diluted with an equal volume of ether, was then

added gradually from a tap funnel, the mixture in the flask being vigorously stirred, and cooled if necessary. The products were isolated in the usual manner.

Most of the experiments concern the use of benzyl chloride, because the preparation of magnesium benzyl chloride is more troublesome than that of the majority of the Grignard reagents.

Phenylethylcarbinol was prepared from benzaldehyde and ethyl bromide. The reaction proceeded without difficulty, and no secondary or decomposition products appeared to be formed; almost the whole of the crude product distilled constantly at $131\text{--}132^\circ/50$ mm., leaving very little residue; the yield of the carbinol was nearly theoretical. During the distillation the formation of water was not observed, and even when distilled under 750 mm. pressure, the carbinol boiled constantly at $210\text{--}211^\circ$ without decomposing.

Benzylmethylethylcarbinol was prepared from methyl ethyl ketone and benzyl chloride; only small quantities were used, but the yield seemed to be satisfactory. On distillation under 747 mm. pressure, the carbinol decomposed, giving off water, and boiling at $215\text{--}225^\circ$. It has been described by Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 228).

Triethylcarbinol was obtained from diethyl ketone and ethyl bromide. During the preparation, colourless crystals, doubtless the additive compound, separated on the sides of the flask. The crude product distilled at $130\text{--}140^\circ/747$ mm. without decomposing, and the yield was at least 60 per cent. of the theoretical. It is described as an oil boiling at $140\text{--}142^\circ$ under atmospheric pressure.

Benzylphenylmethylcarbinol was prepared from magnesium ($1\frac{1}{4}$ atoms), benzyl chloride ($1\frac{1}{4}$ mols.), and acetophenone (1 mol.) in dry ethereal solution. A gentle reaction set in, and continued until all the metal had disappeared. After the ether had been removed, the additive compound was decomposed with water, and the product was distilled under 30 mm. pressure; it did not boil at a constant temperature, but passed over from 170° to 200° , and appeared to be a mixture of the carbinol and the unsaturated hydrocarbon (α -methylstilbene) derived from it. After several redistillations, however, a large proportion of it solidified on being kept for some time, giving the desired carbinol, which was easily obtained in a pure condition by recrystallisation from light petroleum. The compound has been described by Hell (*Ber.*, 1904, **37**, 457).

Benzylethylpropylcarbinol, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CEtPr}\cdot\text{OH}$, was prepared by the interaction of ethyl propyl ketone and benzyl chloride; the yield was only about 60 per cent. of the theoretical, since, besides the carbinol, a rather large proportion of the unsaturated hydro-

carbon, derived from the carbinol by loss of water, was obtained. The carbinol boils at $186^{\circ}/90$ mm., and a sample of the pure compound gave, on analysis, the following results:

0.1824 gave 0.5442 CO_2 and 0.1729 H_2O . $\text{C}=81.3$; $\text{H}=10.5$.

$\text{C}_{13}\text{H}_{20}\text{O}$ requires $\text{C}=81.2$; $\text{H}=10.4$ per cent.

Benzyl dimethylcarbinol could not be obtained by treating magnesium with a mixture of acetone and benzyl chloride, for although acetone reacts vigorously with a prepared solution of a Grignard compound, the presence of the ketone seems to retard or prevent the formation of magnesium benzyl chloride. This preparation was attempted several times, using acetone which had been dried with calcium chloride during several days, and then distilled, and also samples which had been first treated with a small quantity of a solution of the Grignard compound and then decanted; only negative results were obtained. In other experiments the formation of the Grignard compound was first started by the addition of a little benzyl chloride, and then the mixture of acetone and benzyl chloride was added, drop by drop, to the magnesium, but the vigorous action which was in progress soon ceased after a small proportion of the acetone had been added, and could not be made to start again. In a similar manner, the addition of acetone to an ethereal solution of magnesium ethyl bromide, which is reacting vigorously with magnesium, soon brings the interaction to a standstill.

Phenyldibenzylcarbinol was prepared from ethyl benzoate (1 mol.) and benzyl chloride (2 mols.) in presence of magnesium, the reaction proceeding without difficulty. The product was distilled under diminished pressure, and the distillate readily solidified to a hard, pale yellow cake. On recrystallisation from light petroleum, the carbinol was obtained in colourless needles; the yield was 60 per cent. of the theoretical. The compound has been described by Klages (*Ber.*, 1904, **37**, 1456). An attempt was made to prepare phenyl ethyl ketone by adding a mixture of ethyl benzoate (1 mol.) and ethyl bromide (1 mol.) to magnesium, but the product appeared to be a mixture of unchanged ethyl benzoate and phenyldiethylcarbinol.

Dibenzylethylcarbinol, $\text{CEt}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2\cdot\text{OH}$, was prepared from ethyl propionate and benzyl chloride in presence of magnesium and ether. When the ingredients had been mixed, the solution was heated under a reflux condenser for a short time, the ether was distilled off, and the residue heated at 100° during about two hours. The product was isolated in the usual manner, and the yield was good:

0.1717 gave 0.5337 CO_2 and 0.1308 H_2O . $\text{C}=84.8$; $\text{H}=8.5$.

$\text{C}_{17}\text{H}_{20}\text{O}$ requires $\text{C}=85.0$; $\text{H}=8.3$ per cent.

Dibenzylethylcarbinol is a colourless, viscous liquid, boiling at $193^\circ/12$ mm. When cooled in a freezing mixture, it becomes very viscous, but does not crystallise, and when boiled under atmospheric pressure it decomposes slowly with elimination of water.

Diethylstannic Chloride, SnEt_2Cl_2 .

Stannic chloride (1 mol.) was treated with ethyl bromide (1 mol.) in presence of magnesium and ether under the usual conditions with the intention of obtaining a mono-alkyl derivative of tin, but a compound of this type seemed not to be formed, or was produced in small quantities only. The principal product was diethylstannic chloride, which has been described by Pfeiffer (*Ber.*, 1902, **35**, 3306), and which was identified by its melting point as well as by analysis.

α -Bromo- $\alpha\alpha$ -dibenzylpropane, $\text{CEtBr}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2$.

For a purpose outside the scope of this investigation, experiments were made on the preparation of α -bromo- $\alpha\alpha$ -dibenzylpropane, and on the conversion of this compound into $\gamma\gamma$ -dibenzyl-*n*-hexane; as the former operation is successful only under particular conditions, the results are here recorded. Dibenzylethylcarbinol (15 grams) is dissolved in dry ether (80 c.c.), and phosphorus tribromide (35 grams) is added gradually to the solution; the mixture, which becomes warm, is kept at the ordinary temperature for about twenty-four hours, then boiled under a reflux condenser for about an hour; finally the ether is distilled, and the residue is heated at 100° for about two hours. The product, when cold, is poured on ice, the bromide is extracted with ether, and the extract is washed with sodium carbonate solution, which removes phosphorus compounds. From the crude preparation which is obtained by the evaporation of the ethereal solution, the pure bromide is easily isolated by crystallisation from light petroleum. The yield is at least 85 per cent. of the theoretical.

The combined bromine was estimated by boiling the sample with an alcoholic solution of silver nitrate:

0.2861 gave 0.1765 AgBr . $\text{Br}=26.1$.

$\text{C}_{17}\text{H}_{19}\text{Br}$ requires $\text{Br}=26.4$ per cent.

α -Bromo- $\alpha\alpha$ -dibenzylpropane forms large, colourless prisms, and melts at 58 – 59° . It rapidly loses hydrogen bromide when it is heated at about 115° , and it cannot be distilled even under 13 mm. pressure.

Many unsuccessful attempts were made to prepare $\gamma\gamma$ -dibenzyl-*n*-hexane. The bromide was treated with magnesium propyl bromide, and also with propyl bromide and magnesium in presence of ether, but in both cases the qualitative and quantitative analysis of the product showed it to consist principally, if not entirely, of an unsaturated hydrocarbon. An ethereal solution of the bromide was also heated with propyl bromide and sodium, but only the propyl bromide was attacked, and the α -bromo- $\alpha\alpha$ -dibenzylpropane was recovered unchanged.

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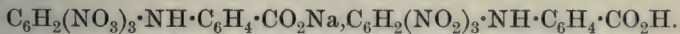
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XXXVIII.—*The Picraminobenzoic Acids and their Salts.*

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SOME years ago, at the suggestion of Dr. G. S. Turpin, one of the authors examined the interaction of the three aminobenzoic acids and picryl chloride in the presence of alkali.

When *o*-aminobenzoic acid was treated in dilute alcoholic solution with the equivalent quantities of picryl chloride and sodium hydroxide, a scarlet, crystalline substance separated on cooling. On repeating the experiment in a solution containing less alcohol, golden-yellow crystals separated on cooling. Analysis showed the latter substance to be free from sodium, and the data agreed with the formula for *o*-picraminobenzoic acid. The scarlet crystals contained sodium, and the substance was shown to be an acid salt of the formula:



Similar results were obtained with *m*-aminobenzoic acid. In concentrated alcoholic solutions, the reaction gave a scarlet acid sodium salt, the analysis of which was in accordance with the above formula. In dilute alcoholic solutions, *m*-picraminobenzoic acid was formed, and separated as a fluffy, yellow mass. With *p*-aminobenzoic acid, only one product was obtained at the time. From concentrated alcoholic solutions, or solutions containing a moderate amount of water, the product of the reaction was *p*-picraminobenzoic acid, which separated in lustrous, yellow

leaflets. The ease with which these salts are hydrolysed is remarkable. Merely crystallising from dilute alcohol is sufficient to hydrolyse them completely to the acids, which separate in a pure state from the solution. The salt of *m*-picraminobenzoic acid is more easily hydrolysed than that of the corresponding ortho-acid. The salts can be crystallised from alcohol containing a little water, without change.

At this stage of the work a paper by Wedekind (*Ber.*, 1900, **33**, 426) appeared, in which a brief account of the preparation and properties of the picraminobenzoic acids was given (*loc. cit.*, p. 431). The alkali salts were stated to crystallise well, and no further reference was made to them. The remarkable character of these salts appears to have been overlooked.

The work described above was discontinued for some time, and has been resumed recently. It has been found that the property of forming acid salts is characteristic of these three acids.

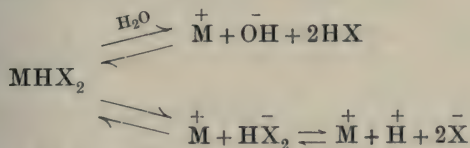
The authors have prepared acid salts of sodium, potassium, ammonium, methylamine, ethylamine, aniline, and pyridine, derived from the *o*-acid; and from the *m*-acid have obtained the corresponding salts of sodium, potassium, methylamine, ethylamine, and guanidine.

The acid salts of potassium and methylamine with the *p*-acid have also been prepared. Most of these acid salts show in a more or less marked degree the property of being hydrolysed by water. Even in the cold, when shaken with excess of water, the salts are gradually decomposed, with complete precipitation of the acid. These salts are not very soluble in water. On the other hand, some alkali salts of the normal type have been prepared, and they differ in character from the acid salts. They are readily soluble in water, and undergo very little hydrolysis even when boiled in aqueous solution. These salts are much more difficult to prepare than the acid salts. This property of forming acid salts would appear to be connected with the tendency of picryl derivatives to form additive compounds with substances the molecules of which contain nuclei of the benzene type. With this idea in view, the molecular weights of the acids were determined in acetone solution. The acids, however, were found to have simple unassociated molecules, so that the complex anions which give rise to the acid salts apparently do not exist to any extent in solutions of the acids. In the presence of a base, however, a normal salt would probably be first formed, and the residual affinity of this would be greater than that of the acid, and thus would favour the formation of the complex anion of the acid salt.

The remarkable behaviour of these salts in the presence of water

or dilute alcohol is to be ascribed mainly to the small solubility of the acids, and their very small affinity constants. The salts are thus easily attacked by water, and the acid is removed from the sphere of action by precipitation as soon as it is formed, so that in the presence of excess of water the hydrolysis proceeds to an end.

When the salt is shaken with water in quantity insufficient for complete hydrolysis, a state of equilibrium is eventually attained. In the solution the salt will probably dissociate electrolytically and hydrolytically, according to the scheme:



Let C_x , C_i , C_w , C_a , C_{OH} be the molecular or ionic concentrations respectively of the simple anion, the complex anion, water, the free acid, and hydroxyl, in the solution.

Also let C_M be the total ionic concentration of the cation of the salt in solution, and C_r the total concentration of the acid radicle in the combined and free state, in the solution. Then, if K_w , K_a , K are respectively the ionic product for water, the dissociation constant of the acid, and the "hydrolysis constant" of the salt, the state of equilibrium in the solution is defined by the following equations:

- $$\begin{array}{ll}
 (1) \quad C_a^2 C_{\text{OH}} = K C_i C_w & (4) \quad C_M + C_H = C_{\text{OH}} + C_i + C_x \\
 (2) \quad C_H C_{\text{OH}} = K_w & (5) \quad C_r = C_a + 2C_i + C_x \\
 (3) \quad C_H C_x = K_a C_a
 \end{array}$$

These equations give the necessary data for finding the concentrations of the various ions and molecules in solution. It is clear at once from (1) that the concentration of the hydroxyl ions in solution should be constant whatever the quantity of salt originally taken, provided the water is not in excess. This fact was verified by a study of the hydrolysis of the acid potassium salt of the *o*-acid in water at 25°. When equilibrium was attained, the constant concentration of the free alkali was found to be 4.36×10^{-6} gram-equivalents per c.c. It follows from equation (2), also, that the concentration of the hydrions is constant. Taking K_w to be 1.2×10^{-20} at 25°, this gave a value for $C_H = 2.77 \times 10^{-15}$ gram-equivalents per c.c.

EXPERIMENTAL.

o-Picraminobenzoic Acid.

For the preparation of this and the isomeric acids, equivalent quantities of picryl chloride (2.5 grams) and the amino-acid (1.4 grams) were separately dissolved in dilute alcohol (1:1), the hot solution mixed, and a dilute alcoholic solution of sodium hydroxide (0.8 gram) stirred into the mixture. On cooling, the picramino-derivative crystallised out. Wedekind's method of using two molecular proportions of amino-acid to one of picryl chloride involves the loss of one molecule of the former, this being converted into the hydrochloride.

o-Picraminobenzoic acid crystallises from alcohol in minute, acicular crystals of a golden-yellow tint, melting at 270° (Wedekind gives 271 — 272°), which are sparingly soluble in water, moderately so in boiling alcohol or acetone, and practically insoluble in ether. The yield of the substance was 2.2 grams. (Found, $N=16.32$. Calc., $N=16.10$ per cent.)

The solubility of the acid in water at 25° was determined:

I. 65.80 grams of solution, saturated at 25° for six hours, gave 0.0244 gram of acid. Solubility = 0.037 per 100 grams of solution.

II. 35.40 grams of solution, saturated at 25° for nine hours, gave 0.0175 gram of acid. Solubility = 0.049 per 100 grams of solution.

Mean solubility = 0.043 gram per 100 grams of solution.

In absolute alcohol at 50° , two experiments gave as the mean result, 0.482 gram per 100 c.c. of solution.

m-Picraminobenzoic Acid.

The yield of this acid, from the quantities given above, was 2.4 grams. On recrystallisation from dilute alcohol, minute, light yellow plates separated at first, but at a lower temperature a fluffy mass of fine needles was obtained. Both kinds of crystals melted sharply at 234° (Wedekind gives 233 — 234°). The substance is readily soluble in acetic acid or acetone, moderately so in methyl and ethyl alcohols, sparingly so in water, and insoluble in ether. (Found, $N=16.03$. Calc., $N=16.10$ per cent.)

The solubility in alcohol at 50° was determined. The mean result of two experiments was 1.200 grams per 100 c.c. of solution.

p-Picraminobenzoic Acid.

The yield of this acid, prepared as above, was 2.6 grams. The pure substance crystallises in pale yellow, spangled leaves, melting at 285° (Wedekind gives 292 — 293°).

It is sparingly soluble in alcohol or acetone, readily so in glacial acetic acid, and practically insoluble in water or ether. It is dissolved by alkalis to a deep red solution. (Found, $N=16.13$. Calc., $N=16.10$ per cent.)

The solubility in alcohol at 50° was determined. The mean of two experiments gave 0.220 gram per 100 c.c. of solution. The molecular weights of the three acids were determined in boiling acetone solution.

Molecular Weights of the Picraminobenzoic Acids.

w = weight of acid.

Δ = elevation of boiling point.

V = volume of solution in c.c.

M = molecular weight.

<i>o</i> -Acid.				<i>m</i> -Acid.				<i>p</i> -Acid.			
<i>w.</i>	<i>V.</i>	Δ .	<i>M.</i>	<i>w.</i>	<i>V.</i>	Δ .	<i>M.</i>	<i>w.</i>	<i>V.</i>	Δ .	<i>M.</i>
0.9568	12.5	0.54°	314	1.188	12.0	0.64°	343	0.4669	15.0	0.20°	346
„	21.0	0.30	337	„	14.0	0.55	343	„	22.0	0.15	314
„	23.5	0.27	334	„	15.5	0.50	341	„	30.5	0.10	340
„	„	„	„	„	17.0	0.46	338	„	„	„	„
Mean.....			328.3	Mean			341.2	Mean..			333.3

The calculated molecular weight for the simple unassociated molecule is in each case 348.

Acid Sodium o-Picraminobenzoate.

For the preparation of this salt, 2.5 grams of picryl chloride were dissolved in the least possible quantity of alcohol, and 1.4 grams of anthranilic acid in dilute alcohol (3: 2). The solutions were mixed while hot, and a solution of 0.8 gram of sodium carbonate in dilute alcohol was rapidly stirred in. The colour of the solution became dark red, and on cooling slightly, minute, scarlet, needle-shaped crystals separated out. The yield was 2.2 grams. The substance was recrystallised from alcohol containing a little water. If dissolved in hot dilute alcohol (1: 1), the acid separates, on cooling, in golden-yellow needles. The substance is slowly hydrolysed to the acid when in contact with cold water. The change is accelerated by shaking or heating. In the presence of excess of water, the change is complete, but, in general, some of the salt remains unchanged, and a state of equilibrium is set up between the salt, acid, and the base in solution. The substance is moderately soluble in water, but sparingly so in alcohol. It is rather more soluble in acetone than in alcohol, and is insoluble in benzene or ether. Excess of alkali easily dissolves the salt to a deep red solution, from which the acid is precipitated on addition of dilute acid. The salt decomposes gradually at 140° , the crystals becoming brown:

0.3201 gave 0.0290 Na_2SO_4 . $\text{Na} = 2.94$.

0.4398 „ 0.0360 Na_2SO_4 . $\text{Na} = 2.65$.

$\text{C}_{26}\text{H}_{15}\text{O}_{16}\text{N}_8\text{Na}$ requires $\text{Na} = 3.20$ per cent.

The salt was also prepared from *o*-picraminobenzoic acid. 3.5 Grams of the acid were dissolved in boiling alcohol, and a solution of 0.3 gram of sodium hydroxide in alcohol containing a little water was stirred into it. A yield of 3 grams of the salt was obtained on cooling.

Acid Potassium o-Picraminobenzoate.

Four grams of *o*-picraminobenzoic acid were dissolved in boiling alcohol, and 3 c.c. ($=0.6$ gram KOH) of a 20 per cent. solution of potassium hydroxide in dilute alcohol (2: 1) were stirred into the solution. The salt was precipitated immediately, and was washed with alcohol and ether. The yield was 3.5 grams. The substance consists of minute, glistening, scarlet crystals, which occur in elongated, six-sided plates. It is moderately soluble in water, and is hydrolysed by it slowly in the cold. On heating, the hydrolysis is rapid, and in presence of excess of water is complete, giving a yellow, powdery precipitate of the acid. It is sparingly soluble in alcohol, and is partly hydrolysed by the hot solvent. In acetone or methyl alcohol the substance is more soluble, but is again hydrolysed a little. It is insoluble in benzene or ether. With alkalis, deep red solutions are obtained, from which the acid is precipitated by dilute acids. As the salt explodes on heating directly with sulphuric acid, the analysis was effected by treating the salt first with hot water, and then with excess of dilute sulphuric acid to precipitate the acid. The filtrate from this was evaporated, and the residue was ignited and weighed in the usual manner:

0.2546 gave 0.0300 K_2SO_4 . $\text{K} = 5.28$.

0.5209 „ 0.0616 K_2SO_4 . $\text{K} = 5.30$.

$\text{C}_{26}\text{H}_{15}\text{O}_{16}\text{N}_8\text{K}$ requires $\text{K} = 5.31$ per cent.

The method of preparation and purification described above is typical for many of these salts, and except where otherwise stated is the method used.

Acid Ammonium o-Picraminobenzoate.

3.5 Grams of *o*-picraminobenzoic acid, treated with 0.12 gram of ammonia, gave 2.8 grams of the salt.

The substance consists of radiating clusters of scarlet needles. It is insoluble in ether, and sparingly soluble in ethyl and methyl alcohols, but readily so in water, and is hydrolysed partly to the acid in the cold. Even alcoholic solutions gave, on partial evaporation, a mixture of acid and salt. The salt can, however, be

crystallised unchanged from alcohol containing a very little ammonia. For the analysis, a weighed quantity was treated with hot water, and then the acid was precipitated by the addition of hydrochloric acid. After filtration, the solution was evaporated with platinum chloride, and the estimation was then completed in the usual manner:

0.3520 gave 0.0840 $(\text{NH}_4)_2\text{PtCl}_6$ and 0.0047 Pt. $\text{NH}_4 = 2.18$.

0.4096 „ 0.0980 $(\text{NH}_4)_2\text{PtCl}_6$ „ 0.0012 Pt. $\text{NH}_4 = 1.99$.

$\text{C}_{26}\text{H}_{19}\text{O}_{16}\text{N}_9$ requires $\text{NH}_4 = 2.52$ per cent.

Silver o-Picraminobenzoate.

1.75 Grams of the acid, treated with 0.9 gram of silver nitrate, gave 1 gram of the dark red salt. It is insoluble in water, alcohol, or ether. For analysis, the salt was decomposed by dilute sulphuric acid in excess. The precipitated acid was removed, and the silver was weighed as the sulphate:

0.2874 gave 0.0947 Ag_2SO_4 . $\text{Ag} = 22.81$.

0.2688 „ 0.0891 Ag_2SO_4 . $\text{Ag} = 22.95$.

$\text{C}_{13}\text{H}_7\text{O}_8\text{N}_4\text{Ag}$ requires $\text{Ag} = 23.68$ per cent.

The salt is thus one of the normal series.

Acid Methylammonium o-Picraminobenzoate.

Three grams of the acid, treated in the usual manner with 0.2 grams of methylamine, gave 3 grams of the salt.

The substance consists of minute, yellowish-red needles, melting and decomposing at $234-235^\circ$. It is partly soluble in water, and is hydrolysed by it readily to the acid, which is precipitated as a yellow powder. It is sparingly soluble in methyl and ethyl alcohols, and is insoluble in benene or ether.

With potassium hydroxide, a deep red solution is obtained, from which the methylamine is not evolved so readily as from an equivalent solution of methylamine hydrochloride:

0.1978 gave 29.9 c.c. N_2 (moist) at 18.8° and 760 mm. $\text{N} = 17.4$.

0.9471 „ 0.2556 $(\text{NH}_3\text{Me})_2\text{PtCl}_6$ and 0.0127 Pt. $\text{NH}_2\text{Me} = 4.02$.

$\text{C}_{27}\text{H}_{21}\text{O}_{16}\text{N}_9$ requires $\text{N} = 17.34$; $\text{NH}_2\text{Me} = 4.26$ per cent.

Acid Ethylammonium o-Picraminobenzoate.

3.5 Grams of o-picraminobenzoic acid, treated in alcoholic solution with 0.34 gram of ethylamine, gave 2.5 grams of the salt.

The crystals are short, dark red prisms, crystallising in compact, radiating clusters. They melt and decompose at 242° , and are soluble in water, but are partly hydrolysed to the acid. Alkalis dissolve the salt to a deep red solution, but the ethylamine is not

liberated with the usual readiness on warming. In methyl and ethyl alcohols the substance is sparingly soluble, and if such solutions are partly evaporated, a mixture of acid and salt separates. The substance is readily soluble in acetone with partial decomposition, and is insoluble in ether. Dilute acids instantly precipitate the acid from a solution of the salt:

0.6418 gave 0.1700 $(\text{NH}_3\text{Et})_2\text{PtCl}_6$ and 0.0194 Pt. $\text{NH}_2\text{Et}=6.23$.

0.3689 „ 0.1031 $(\text{NH}_3\text{Et})_2\text{PtCl}_6$ „ 0.0053 Pt. $\text{NH}_2\text{Et}=5.68$.

$\text{C}_{28}\text{H}_{23}\text{O}_{16}\text{N}_9$ requires $\text{NH}_2\text{Et}=6.07$ per cent.

Acid Aniline o-Picraminobenzoate.

3.5 Grams of *o*-picraminobenzoic acid were dissolved in the smallest possible quantity of cold aniline. After several days, a mass of reddish-yellow crystals separated. These crystals were washed repeatedly with alcohol and with ether in the cold. The yield was 2 grams. The substance consists of reddish-yellow prisms, crystallising in compact masses formed of radiating clusters of crystals. It darkens just below the melting point, and melts and decomposes at $264-265^\circ$. It is soluble in water, and is easily hydrolysed by it to the acid. Methyl and ethyl alcohols dissolve the substance sparingly; it is insoluble in ether, and readily soluble in aniline or potassium hydroxide solution:

0.3212 gave 0.0386 Pt. $\text{NH}_2\text{Ph}=11.47$.

0.3538 „ 0.0424 Pt. $\text{NH}_2\text{Ph}=11.44$.

$\text{C}_{32}\text{H}_{23}\text{O}_{16}\text{N}_9$ requires $\text{NH}_2\text{Ph}=11.78$ per cent.

Acid Pyridine o-Picraminobenzoate.

2.5 Grams of *o*-picraminobenzoic acid were dissolved in 2.2 grams of pyridine. After several days, a mass of crystals had formed. The product was washed repeatedly with ether. The yield was 1.4 grams. The crystals are small, yellowish-red, compact, six-sided tables. On heating, the substance loses pyridine at about 140° , and the residue melts at 269° (pure acid 270°). The substance is easily decomposed by water, and also by methyl and ethyl alcohols, acetone, or amyl alcohol, giving the acid. It is insoluble in ether, and has a slight odour of pyridine:

0.2812 gave 0.0364 Pt. $\text{C}_5\text{H}_5\text{N}=10.67$.

0.3238 „ 0.0410 Pt. $\text{C}_5\text{H}_5\text{N}=10.00$.

$\text{C}_{31}\text{H}_{21}\text{O}_{16}\text{N}_9$ requires $\text{C}_5\text{H}_5\text{N}=10.20$ per cent.

Acid Sodium m-Picraminobenzoate.

This salt was prepared as described above for the corresponding ortho-salt. 2.5 Grams of picryl chloride, 1.7 grams of *m*-amino-

benzoic acid, and 1.2 grams of sodium hydroxide yielding 2.1 grams of the crude product.

It consists of scarlet, elongated plates, not so dark in colour as the ortho-salt. The crystals are somewhat hygroscopic, and are easily hydrolysed by water or by dilute alcohol to the corresponding acid. They are sparingly soluble in alcohol, and insoluble in ether:

0.2874 gave 0.0262 Na_2SO_4 . $\text{Na}=2.95$.

0.3703 „ 0.0358 Na_2SO_4 . $\text{Na}=3.13$.

$\text{C}_{26}\text{H}_{15}\text{O}_{16}\text{N}_8\text{Na}$ requires $\text{Na}=3.20$ per cent.

Acid Potassium m-Picraminobenzoate.

1.25 Grams of picryl chloride and 0.7 gram of *m*-aminobenzoic acid were separately dissolved in the least quantity of alcohol, and then a large excess of potassium acetate was stirred into the mixed solutions. After some time, the product was removed and treated as in previous cases. The yield was 1 gram. The substance consists of long, red needles, sparingly soluble in methyl and ethyl alcohols, insoluble in ether, soluble in water, and very easily hydrolysed by it to the acid. It cannot be recrystallised from the usual solvents, owing to the precipitation of the acid with the salt:

0.3370 gave 0.0412 K_2SO_4 . $\text{K}=5.48$.

0.7168 „ 0.0872 K_2SO_4 . $\text{K}=5.33$.

$\text{C}_{26}\text{H}_{15}\text{O}_{16}\text{N}_8\text{K}$ requires $\text{K}=5.31$ per cent.

Potassium m-Picraminobenzoate.

3.5 Grams of *m*-picraminobenzoic acid were dissolved in boiling alcohol, and 0.8 gram of potassium hydroxide dissolved in dilute alcohol was stirred into the hot solution. After a short time, the reaction mixture was cooled in ice and salt to -10° and filtered. In a few days, crystals had separated from the filtrate, and these were collected and washed with alcohol and ether. The yield was 1.9 grams. The substance consists of brilliant pale yellow crystals, and it is sparingly soluble in alcohol and insoluble in ether, but readily so in water to an orange solution. Even after boiling this solution, there is only the faintest indication of hydrolysis to the acid. The acid is precipitated at once on the addition of dilute acid:

0.4595 gave 0.1064 K_2SO_4 . $\text{K}=10.38$.

0.4218 „ 0.1003 K_2SO_4 . $\text{K}=10.66$.

$\text{C}_{13}\text{H}_7\text{O}_8\text{N}_4\text{K}$ requires $\text{K}=10.10$ per cent.

The Acid Methylammonium m-Picraminobenzoates.

2.5 Grams of picryl chloride and 1.4 grams of *m*-aminobenzoic acid were separately dissolved in boiling alcohol. The solutions were mixed, and 2 c.c. of a 33 per cent. methylamine solution added. The solution was well cooled, filtered, and set aside. In a few days two kinds of crystals had separated. The one kind were dark red and transparent, the others were yellowish-red and opaque. These two salts were separated mechanically. Good separation was possible on account of the size of the clusters of crystals.

The dark red crystals consisted of compact tables, crystallising in radiating clusters. The substance has no definite melting point, owing to decomposition on heating. It is completely soluble in hot water to a dark red solution, sparingly soluble in alcohol, and insoluble in ether. The yield was 1.4 grams.

The yellowish-red, opaque crystals also consisted of compact tables, but these melted fairly sharply at 164—166°, with decomposition. This salt is also completely soluble in hot water to a red solution. It is sparingly soluble in alcohol, and insoluble in ether. The yield was 0.9 gram. Analysis showed that both salts have the same composition, and are acid salts:

A. Dark red salt; no definite melting point.

1.3479 gave 0.4031 $(\text{NH}_3\text{Me})_2\text{PtCl}_6$ and 0.0041 Pt. $\text{NH}_2\text{Me}=4.03$.

B. Opaque, yellowish-red salt, melting at 164—166°.

0.4494 gave 0.1214 $(\text{NH}_3\text{Me})_2\text{PtCl}_6$ and 0.0056 Pt. $\text{NH}_2\text{Me}=3.95$.

$\text{C}_{27}\text{H}_{21}\text{O}_{16}\text{N}_9$ requires $\text{NH}_2\text{Me}=4.26$ per cent.

Acid Ethylammonium m-Picraminobenzoate.

2.5 Grams of picryl chloride, 1.4 grams of *m*-aminobenzoic acid, and 2.5 c.c. of 33 per cent. ethylamine solution, treated as in the previous case, yielded 3 grams of the salt, which was recrystallised from weak alcoholic ethylamine.

The substance crystallises in bright yellow plates, melting at 188°, which are sparingly soluble in alcohol to a red solution, insoluble in ether, and soluble in hot water to a dark red solution. When crystallised from pure alcohol, the salt is decomposed slightly:

0.6135 gave 0.2035 $(\text{NH}_3\text{Et})_2\text{PtCl}_6$ and 0.0036 Pt. $\text{NH}_2\text{Et}=6.23$.

0.3446 „ 0.0954 $(\text{NH}_3\text{Et})_2\text{PtCl}_6$ „ 0.0105 Pt. $\text{NH}_2\text{Et}=6.38$.

$\text{C}_{28}\text{H}_{23}\text{O}_{16}\text{N}_9$ requires $\text{NH}_2\text{Et}=6.07$ per cent.

Acid Guanidine m-Picraminobenzoate.

3.5 Grams of *m*-picraminobenzoic acid and 0.6 gram of guanidine carbonate, treated by the usual method, gave 2.5 grams of the salt.

The substance is soluble in hot water to a dark red solution without precipitation of the acid. It is sparingly soluble in alcohol, insoluble in ether, and melts at 246° :

0.3676 gave 0.1044 $(\text{CH}_5\text{N}_3)_2\text{H}_2\text{PtCl}_6$ and 0.0089 Pt. $\text{CH}_5\text{N}=7.82$.

$\text{C}_{27}\text{H}_{21}\text{O}_{16}\text{N}_{11}$ requires $\text{CH}_5\text{N}=7.81$ per cent.

Sodium p-Picraminobenzoate.

1.2 Grams of *p*-picraminobenzoic acid were dissolved in alcohol, to which 10 per cent. of acetone had been added. To the hot solution was added gradually 3.0 c.c. of a 5 per cent. solution of sodium hydroxide in dilute alcohol. After some time, the crystals were collected. The yield was 0.9 gram of a brownish-yellow substance, which crystallises in minute needles. These settled out in tufts on the sides of the vessel. The substance is moderately soluble in alcohol, and insoluble in ether. It is readily and completely soluble in water without any precipitation of the acid. The aqueous solution is of a dark red colour, and the acid is immediately precipitated from it on the addition of an acid:

0.2528 gave 0.0442 Na_2SO_4 . $\text{Na}=5.66$.

0.4179 „ 0.0759 Na_2SO_4 . $\text{Na}=5.88$.

$\text{C}_{13}\text{H}_7\text{O}_8\text{N}_4\text{Na}$ requires $\text{Na}=6.21$ per cent.

Acid Potassium p-Picraminobenzoate.

1.75 Grams of *p*-picraminobenzoic acid, treated with 0.21 gram of potassium hydroxide in a 10 per cent. solution of acetone in alcohol, yielded 0.9 gram of the salt.

The substance consists of buff-coloured needles, sparingly soluble in alcohol, and insoluble in ether. It is moderately soluble in hot water to a dark red solution, and is partly hydrolysed to the acid:

0.4024 gave 0.0485 K_2SO_4 . $\text{K}=5.40$.

0.4314 „ 0.0512 K_2SO_4 . $\text{K}=5.70$.

$\text{C}_{26}\text{H}_{15}\text{O}_{16}\text{N}_8\text{K}$ requires $\text{K}=5.31$ per cent.

Ammonium p-Picraminobenzoate.

1.5 Grams of *p*-picraminobenzoic acid, treated in boiling alcohol (200 c.c.) with 2 c.c. of *N*-ammonia solution, yielded, on cooling, 0.7 gram of the salt. The substance crystallises in very dark red needles.

It becomes pale yellow on heating to 210° , and has no well-defined melting point, owing to decomposition on heating. It is sparingly soluble in alcohol, insoluble in ether, and completely soluble in

water to a dark red solution. Analysis showed the substance to be the normal salt:

0.1490 gave 0.0760 $(\text{NH}_4)_2\text{PtCl}_6$ and 0.0025 Pt. $\text{NH}_4 = 4.44$.

0.2974 „ 0.1705 $(\text{NH}_4)_2\text{PtCl}_6$ „ 0.0020 Pt. $\text{NH}_4 = 4.76$.

$\text{C}_{13}\text{H}_{11}\text{O}_8\text{N}_5$ requires $\text{NH}_4 = 4.93$ per cent.

Acid Methylammonium p-Picraminobenzoate.

1.75 Grams of *p*-picraminobenzoic acid were suspended in 70 c.c. of boiling alcohol, and 0.15 gram of methylamine in dilute alcohol was added. The acid dissolved, and in a few days long, slender, reddish-golden coloured needles had separated. The yield was 1.2 grams, and the crystals melted at 204° . They are sparingly soluble in alcohol, insoluble in ether, and readily soluble in warm water to a dark red solution. Analysis showed the substance to be the acid salt:

0.3876 gave 0.1345 $(\text{NH}_3\text{Me})_2\text{PtCl}_6$ and 0.0054 Pt. $\text{NH}_2\text{Me} = 4.98$.

0.3764 „ 0.0507 Pt. $\text{NH}_2\text{Me} = 4.44$.

$\text{C}_{27}\text{H}_{21}\text{O}_{16}\text{N}_9$ requires $\text{NH}_2\text{Me} = 4.26$ per cent.

Hydrolysis of the Acid Potassium Salt of o-Picraminobenzoic Acid.

The salt was stirred with water in a solubility apparatus at 25° for eight hours. Care was taken that the water was not in excess. The residue, on analysis, was in each case found to contain unaltered salt.

After eight hours, some of the solution was filtered off at the temperature of the thermostat and removed for analysis. The acid was precipitated by a few drops of concentrated hydrochloric acid, collected, and dried, first at 100° and then at 150° . It was then weighed. The filtrate from this treatment was practically colourless, showing that the precipitation of the acid was practically complete. It was evaporated carefully with sulphuric acid, and the potassium in it was estimated as K_2SO_4 . From the weights of the acid and the potassium sulphate, the total amounts of the base and the acid radicle in solution were obtained. The concentrations of the hydroxidions and hydrions were calculated from the formulæ:

$$(1) \text{C}_{\text{OH}} = \text{C}_m - \frac{1}{2}(\text{C}_r - \text{C}_a). \quad (2) \text{C}_\text{H} = \frac{\text{K}_w}{\text{C}_{\text{OH}}}$$

The following are the results obtained in three different experiments:

Temperature = 25° .

Solubility of acid = 1.244×10^{-6} equivalents per c.c.

Ionic product for water, $K_w = 1.20 \times 10^{-20}$.

Weight of solution.	K_2SO_4 .	Acid.	$C_m \times 10^6$.	$C_r \times 10^6$.	$COH \times 10^6$.	$CH \times 10^{15}$.
29.06	0.0166	0.0586	6.566	5.794	4.291	2.800
25.95	0.0148	0.0522	6.555	5.775	4.290	2.860
26.70	0.0156	0.0527	6.725	5.675	4.510	2.662
Mean values ...					4.363	2.774

It will be noted that the constant concentration of the alkali in solution is very small, and is, roughly, $N/250$.

Summary.

1. The picraminobenzoic acids form a characteristic series of acid salts, containing two equivalents of the acid radicle to one equivalent of the base.

2. These salts are only moderately soluble in water, and are generally easily hydrolysed, with precipitation of the acid, leaving alkali in solution. The hydrolysis is complete in presence of excess of water, and takes place slowly even in the cold. When the salt is in excess, a state of equilibrium is set up between the salt, acid, and base in solution.

3. The normal salts obtained are readily soluble in water, and show little signs of hydrolysis even on boiling with water.

4. The picraminobenzoic acids are sparingly soluble in water, have very feeble acid properties, and are non-associated in solution.

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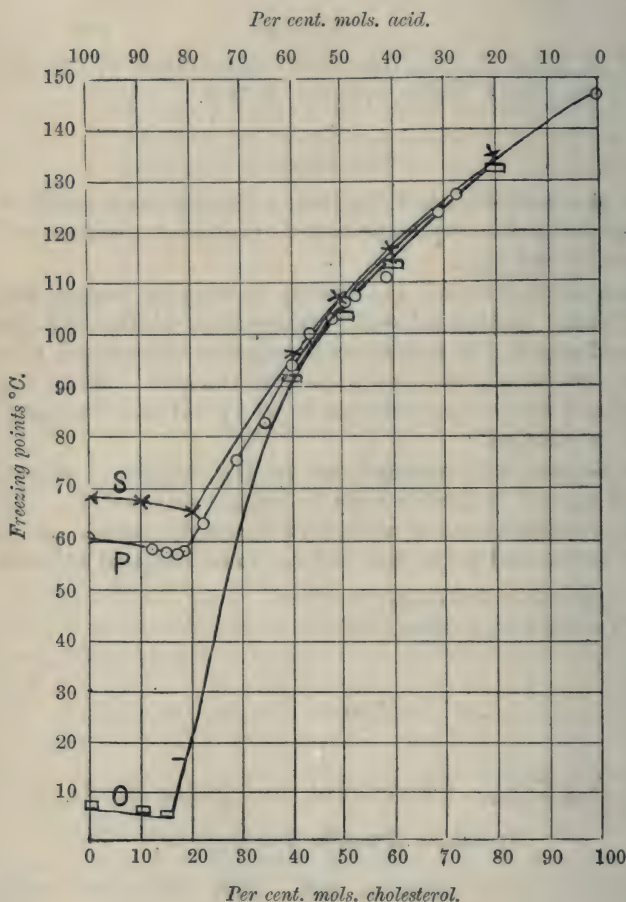
XXXIX.—Cholesterol and Fatty Acids.

By JAMES RIDDICK PARTINGTON.

BENEKE (*Ann. Chem. Pharm.*, 1863, **127**, 105) observed that cholesterol which had been crystallised from hot acetic acid "differs from ordinary cholesterol." Lindenmeyer (*J. pr. Chem.*, 1863, **90**, 321, 331) states that he had been informed by Dr. Zalesky that cholesterol crystallises in thin needles from acetic acid, but in plates from other solvents. He prepared crystals in this way, pressed them between filter-paper, and dried "at the ordinary temperature." They melted at 110° , and in two experiments the losses at

120° were 12·7 and 13·7 per cent. The calculated loss for $C_{26}H_{44}O, C_2H_4O_2$ was 13·9 per cent., and Lindenmeyer concluded that the substance was an equimolecular compound, the defect in the loss being put down to difficulties in removing the whole of the acetic acid.

F. C. Moore (*Med. Chron.*, 1908, p. 204) quotes the above experi-



ments as evidence for the existence of a compound of cholesterol and acetic acid, and repeated some of the tests. The evidence was:

- (1) The different melting points of pure cholesterol and the "compound."
- (2) The change of melting point after treating with water, alcohol, or alkalis.

(3) The change of crystalline form after complete dissolution in alcohol, and crystallisation.

Moore and C. P. White (*Med. Chron.*, 1908; *J. Path. Bact.*, 1908, 13, 5) then extended this conclusion (it appears to the author without any satisfactory experimental proof) to other fatty acids, such as palmitic and stearic; the latter author stating that "cholesterol has the remarkable character of being able to take up fatty acids to form loose combinations which are not the esters. Presumably in these combinations the acids exist as 'acids of crystallisation.'"

Since the evidence in the case of acetic acid is not conclusive, and in the cases of stearic and palmitic acids is wanting, I decided, on the suggestion of Dr. A. Lapworth, to make further experiments on the matter. The first cases investigated were the mixtures of cholesterol with palmitic, stearic, and oleic acids.

The method used was to determine the temperatures at which the first portion of solid separated from fluid mixtures of the two components. If any definite solid compound is produced at these temperatures, the curve representing temperature of separation as a function of the fractional molecular composition of the mixture will either exhibit a maximum with two minima corresponding with the so-called eutectics, or mixtures of the solid components, or else will show a sharp break in one branch of the two systems of curves descending to a single eutectic point. If, on the contrary, the substance separating is invariably one of the pure components, and, at a single point, both pure components side by side, the system will consist of two unbroken curves meeting in a eutectic point. The existence of solid solutions, that is, of homogeneous crystals containing both components in proportions which are continuous functions of the proportions existing in the fused mass, has not been suggested, and the work here described has not given any indication that this is to be inferred.

EXPERIMENTAL.

Freezing-point Experiments.

Apparatus.—The inner tube of a Beckmann freezing-point apparatus was surrounded by a wide test-tube to serve as an air-jacket. The substances were weighed directly into this tube, and fused by careful heating with a flame. The cork, through which passed a thermometer and a platinum stirrer, was then fitted on, the whole placed in the air-jacket, and the temperature at which solid began to separate was determined.

In no experiment was there any indication of a fluid crystal phase; the mixture remained perfectly clear until freezing com-

menced, when the separating substance was distinctly seen to consist of small solid crystals dispersed through the still liquid mass. No moisture was at any time evolved, and the colour, even at the high temperatures, was never darker than a pale amber-yellow, indicating an absence of decomposition.

Materials.—The cholesterol and the fatty acids were pure specimens supplied by Kahlbaum. The oleic acid, which was quite colourless, was frozen out and kept on a porous tile in the ice-chest for twelve hours. It was then allowed to melt in a vacuum desiccator over calcium chloride. The purified acid melted at $6\cdot5^{\circ}$; higher melting points (14° according to Gottlieb, *Annalen*, 1846, 57, 38) have been recorded, but there is no reason to believe that the sample used was impure. The cholesterol was dried by heating in an air-oven to 110° for some time, and was kept in a desiccator. The palmitic and stearic acids were used directly.

Results.—The tables and accompanying curves show that, when liquid mixtures of cholesterol with palmitic, stearic, and oleic acids, in any proportions, are cooled, the solids separating are invariably one of the pure components, or a mechanical mixture of both pure components. Within the whole range of concentrations and temperatures investigated, there is no evidence of the existence of a solid compound of cholesterol with any one of the acids.

The experiments do not exclude the possibility that in some cases solid compounds may exist at the ordinary temperature, but no substance of this type has been detected. The existence of these, or of solid solutions, could be decided by an examination of the cooling curves over a large range of temperature. Solids of approximately constant composition may doubtless be obtained on cooling solutions of cholesterol and fatty acids saturated with both components, or by other means, but the conclusion that the masses are chemical compounds requires stringent proof, which does not appear yet to have been adduced.

TABLE I.

Palmitic Acid + Cholesterol.

Palmitic acid, per cent.	Cholesterol, per cent.	Molecules of acid, per cent.	Freezing point.
100.0	0.0	100.0	$60\cdot0^{\circ}$
83.3	16.7	88.2	58.5
80.0	20.0	85.9	57.5
76.9	23.1	83.3	57.0
74.0	26.0	81.1	57.25
68.9	31.1	74.0	61.1
64.5	35.5	73.2	65.0
62.0	38.0	71.1	73.25
58.8	41.2	65.4	82.5

TABLE I (*continued*).*Palmitic Acid + Cholesterol.*

Palmitic acid, per cent.	Cholesterol, per cent.	Molecules of acid, per cent.	Freezing point.
50.0	50.0	60.0	94.0
48.5	51.5	58.5	97.0
46.1	53.9	56.2	100.0
43.8	56.2	53.9	100.5
42.3	57.7	52.5	103.0
41.5	58.5	51.5	106.0
39.1	60.9	49.2	106.5
37.9	62.1	47.9	107.0

Second Series.

50.0	107.0
40.8	111.0
31.7	124.0
27.8	127.0
0	147.0

TABLE II.

Stearic Acid + Cholesterol.

Molecules of cholesterol, per cent.	Molecules of acid, per cent.	Freezing point.
0	100	68.5°
10	90	67.0
20	80	65.0
40	60	91.4
50	50	104.7
60	40	115.0
80	20	134.0
100	0	147.0

TABLE III.

Oleic Acid + Cholesterol.

Molecules of cholesterol, per cent.	Molecules of acid, per cent.	Freezing point.
0	100	6.5°
10	90	6.0
15	85	5.0
20	80	64.0
40	60	95.9
50	50	107.1
60	40	116.4
80	20	134.0

(The mixture 15: 85 solidified completely at 5.0°, and was therefore the eutectic.)

Cholesterol and Acetic Acid; Cholesterol and Propionic Acid.

Some experiments have been made with these systems, but the results have proved inconclusive, since the melting points of the supposed "compounds" corresponded with the points on the freezing curves for mixtures, yet the loss of weight on heating and the acidity were in each case approximately those required by the formulæ: $C_{27}H_{46}O$, $C_2H_4O_2$, $C_{27}H_{46}O$, $C_3H_6O_2$.

This case can be decided by an examination of the vapour-pressure curves during continual withdrawal of the volatile component, and some experiments, the results of which will shortly be communicated, are in progress to settle this point.

Colloidal Cholesterol.

During the course of the work it was observed that a solution of cholesterol in alcohol gave a colloidal solution when added in small quantities to water, with stirring. The alcohol was removed by dialysis, and the colloidal solution has been kept for three months without very much deposition of cholesterol. It was immediately precipitated by mineral acids and alkalis (but not by ammonia), and by ferric, platinic, barium, and calcium chlorides; by zinc, copper, magnesium, and ferrous sulphates; cadmium nitrate, and oxalic acid. Acetic acid and silver nitrate did not precipitate it, but increased the size of the particles. Potassium iodide rendered the solution less opalescent.

O. Porges and E. Neubauer (*Biochem. Zeitsch.*, 1908, **7**, 152) prepared a colloidal solution of cholesterol by adding a solution of cholesterol in acetone to water and dialysing. They examined in detail its precipitation by salts, and their results are in agreement with the above. They also concluded that it was an anodic suspensoid.

The solution described above is also an anodic colloid; it was found that cholesterol wandered to the anode in a cataphoresis experiment. Further, the precipitates with ferric chloride and calcium chloride, after washing with hot water, gave, on heating with dilute nitric acid, solutions which contained the cations, but no trace of anion. The precipitate with hydrochloric acid, after washing, did not contain a trace of anion, and on prolonged washing passed again into colloidal solution.

In conclusion, I desire to thank Dr. Lapworth for the interest he has displayed during the course of the work.

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UNIVERSITY OF MANCHESTER.

XL.— α -Amino- α -phenylacetamide and Some of its Derivatives.

By CHARLES HUGH CLARKE and FRANCIS FRANCIS.

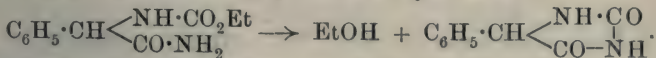
ALTHOUGH Tiemann and Friedländer (*Ber.*, 1881, **14**, 1968) were unable to prepare α -amino- α -phenylacetamide in a pure state from its hydrochloride, we have found the base is stable, and may be easily obtained from mandelonitrile. The action of alcoholic ammonia on the aldehydecyanohydrins results in the formation of the α -amino-nitriles, but if the reaction is carried out in the presence of potassium hydroxide, partial saponification of the nitrile group takes place; and, if benzaldehydecyanohydrin is used, α -amino- α -phenylacetamide is formed, thus:



The isolation of the base from the other products of the reaction is difficult, but if the decomposition is carried out in the presence of benzaldehyde, the well crystalline *benzylidene* derivative can be readily obtained to the extent of about 65 per cent. of the cyanohydrin taken, and α -amino- α -phenylacetamide is best prepared from it by treating it with phenylhydrazine, when the separation of the resulting benzaldehydephenylhydrazone from the base is easily carried out, and a quantitative yield obtained.

α -Amino- α -phenylacetamide is characterised by the readiness with which it condenses with aromatic aldehydes, forming products of the type $\text{C}_6\text{H}_5\cdot\text{CH}(\text{N}:\text{CHR})\cdot\text{CO}\cdot\text{NH}_2$. A similar reaction takes place with acetoacetic ester and ethylacetoacetic ester, but not with the diethyl derivative.

Greater interest lies in the ease with which the five-membered ring, phenylhydantoin, can be formed from the base. The carbethoxy-compound gives an 85 per cent. yield of phenylhydantoin when treated with alcoholic potassium hydroxide:

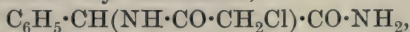


The ease with which the base and its carbethoxy-derivative can be prepared renders this the best method for the preparation of this substance.

Corresponding experiments with α -amino- α -p-methoxyphenylacetamide showed that this also lent itself readily to the formation of p-methoxyphenylhydantoin.

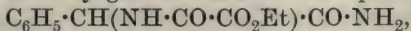
As compared with the ease with which five-membered rings of the above type can be formed is the difficulty experienced in the preparation of any six-membered heterocyclic derivative.

Thus, it was not found possible to obtain a closed ring substance from the interaction of glyoxal and α -amino- α -phenylacetamide. Further, although chloroacetyl chloride gave a good yield of the corresponding chloroacetyl derivative,



it was again not found possible to eliminate hydrogen chloride, and form the six-membered closed chain.

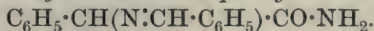
Ethyl oxalate readily gives a condensation product,



but this, on treatment with alcoholic potassium hydroxide or sodium ethoxide, gives the alkali salt of the corresponding acid, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{NH}_2$, and from this substance and its previously-mentioned ethyl ester we were unable to form any cyclic derivative.

EXPERIMENTAL.

α -Benzylideneamino- α -phenylacetamide,



Ten grams of benzaldehydecyanohydrin and 7 grams of benzaldehyde are dissolved in a small quantity of alcohol, and treated with a mixture of 10 c.c. of a 15 per cent. solution of potassium hydroxide with 10 c.c. of aqueous ammonia (D 0.880).

Sufficient alcohol is then added to give a clear solution. Reaction commences at once, and it is necessary to add small quantities of alcohol from time to time to keep the liquid clear.

After twelve hours, the crystalline condensation product which has separated is collected, washed with ether, and recrystallised from benzene. From this solvent 10 to 12 grams separate on cooling, consisting of colourless plates, melting at 120–121°, insoluble in water, but soluble in hot benzene or alcohol:

0.1842 gave 0.0991 H_2O and 0.5126 CO_2 . $\text{C}=75.9$; $\text{H}=5.98$.

0.1760 „, 17.7 c.c. N_2 at 17° and 752 mm. $\text{N}=11.6$.

$\text{C}_{15}\text{H}_{14}\text{ON}_2$ requires $\text{C}=75.6$; $\text{H}=5.90$; $\text{N}=11.8$ per cent.

α -Amino- α -phenylacetamide, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}_2$.

The hydrochloride of this base, previously described by Tiemann and Friedländer, is readily obtained by the action of hydrochloric acid on the benzylidene derivative just described.

As this salt is readily soluble only in hot water, a hot solution must be treated with aqueous potassium hydroxide in order to obtain the base. This treatment results in a partial saponification, and the method consequently gives only a very small quantity of α -amino- α -phenylacetamide. In this probably lies the explanation for the supposed instability of this base.

On the other hand, the *tartrate* is readily soluble in water, and can be obtained by the decomposition of the benzylidene derivative with a solution of tartaric acid. On removal of the resulting benzaldehyde with ether, the base can be precipitated from a concentrated solution in the cold by means of potassium hydroxide. It may be mentioned here that the *tartrate* does not lend itself to the separation of the base into its optical components.

The best method for the isolation of the substance in question consists in warming the benzylidene derivative with the calculated amount of phenylhydrazine in benzene solution. The resulting α -amino- α -phenylacetamide is only sparingly soluble in this medium, and separates first. On cooling, the benzaldehydephenylhydrazone crystallises out, and from this a further amount of base may be extracted by warm water. By this method, a yield of 90 per cent. of the base may be obtained.

α -Amino- α -phenylacetamide is readily soluble in water or alcohol, sparingly so in ether, and almost insoluble in benzene. It is best recrystallised from a mixture of benzene and alcohol, from which it separates on cooling in colourless plates, melting at 130° . Its aqueous solution gives a strongly alkaline reaction, and may be evaporated to dryness without decomposition taking place:

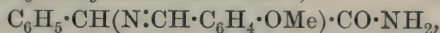
- (1) 0.2024 gave 0.4809 CO_2 and 0.1220 H_2O . $\text{C} = 64.8$; $\text{H} = 6.7$.
0.1920 „ 31.0 c.c. N_2 at 16° and 758 mm. $\text{N} = 18.8$.
 - (2) 0.1620 „ 0.3819 CO_2 and 0.0977 H_2O . $\text{C} = 64.3$; $\text{H} = 6.7$.
0.1524 „ 24.8 c.c. N_2 at 18° and 750 mm. $\text{N} = 18.6$.
- $\text{C}_8\text{H}_{10}\text{ON}_2$ requires $\text{C} = 64.0$; $\text{H} = 6.7$; $\text{N} = 18.6$ per cent.

α -Amino- α -phenylacetamide readily gives condensation products with aromatic aldehydes similar to the benzaldehyde derivative previously mentioned. These may be prepared in quantitative yield by warming together molecular quantities of the aldehyde with the base in alcoholic solution.

The *salicylidene* derivative, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{CO} \cdot \text{NH}_2$, when recrystallised from hot alcohol, melts at 150° :

- 0.2116 gave 0.5506 CO_2 and 0.1140 H_2O . $\text{C} = 70.9$; $\text{H} = 5.98$.
 $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 70.9$; $\text{H} = 5.51$ per cent.

The *o*-methoxybenzylidene derivative,



is not formed so easily as the preceding. When recrystallised from alcohol, it melts at 174 — 175° :

- 0.2180 gave 20.4 c.c. N_2 at 12° and 750.5 mm. $\text{N} = 10.9$.
 $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{N} = 10.5$ per cent.

The *p*-methoxybenzylidene derivative was prepared by heating the alcoholic solution of anisaldehyde and base for some hours

before the condensation was complete. It crystallises from hot alcohol in colourless needles, melting at 164—165°:

0.1894 gave 17.8 c.c. N_2 at 17° and 762 mm. $N=10.9$.

$C_{16}H_{16}O_2N_2$ requires $N=10.5$ per cent.

Ethyl β -Carbamylphenylmethylaminocrotonate,
 $NH_2 \cdot CO \cdot CHPh \cdot NH \cdot CMe \cdot CH \cdot CO_2Et$.

When molecular quantities of acetoacetic ester and the base are heated together in alcoholic solution with a trace of sodium ethoxide, a quantitative yield of the condensation product separates out on the addition of water. It is only sparingly soluble in benzene or ether, and best recrystallised from dilute alcohol, from which it separates in colourless needles, melting at 150°:

0.2814 gave 27.2 c.c. N_2 at 14° and 738 mm. $N=11.0$.

$C_{14}H_{18}O_3N_2$ requires $N=10.7$ per cent.

Ethylacetoacetic ester gave a corresponding derivative, melting at 132°, which was not analysed, but no condensation product could be obtained from diethylacetoacetic ester.

Preparation of Phenylhydantoin.

Both the carbomethoxy- and carbethoxy-derivatives of aminophenylacetamide were prepared and investigated in order to find which condensed more readily to the hydantoin.

α -Carbomethoxyamino- α -phenylacetamide,

$C_6H_5 \cdot CH(NH \cdot CO_2Me) \cdot CO \cdot NH_2$,

is readily obtained in quantitative yield by shaking a solution of the base in water containing sodium carbonate with methyl chloroformate. It crystallises from dilute alcohol in colourless plates, melting at 210°, and is readily soluble in hot water or alcohol:

0.1356 gave 16.6 c.c. N_2 at 18° and 751 mm. $N=13.9$.

$C_{10}H_{12}O_3N_2$ requires $N=13.4$ per cent.

α -Carbethoxyamino- α -phenylacetamide,

$C_6H_5 \cdot CH(NH \cdot CO_2Et) \cdot CO \cdot NH_2$,

may be prepared in a similar manner to the previous derivative by employing ethyl chloroformate. It is only sparingly soluble in the ordinary organic solvents, and is best recrystallised from dilute pyridine, from which it separates in small, brilliant needles, melting at 202°:

0.2664 gave 30.4 c.c. N_2 at 22° and 760 mm. $N=12.9$.

$C_{11}H_{14}O_3N_2$ requires $N=12.6$ per cent.

When this derivative is warmed with dilute hydrochloric acid, it dissolves, and, on cooling, *α -carbethoxyamino- α -phenylacetic acid*, melting at 118°, crystallises out:

0.1418 gave 8.4 c.c. N_2 at 19° and 749.5 mm. $N=6.7$.

$C_{11}H_{13}O_4N$ requires $N=6.3$ per cent.

No difference was found in the ease with which the carbomethoxy- or carbethoxy-derivative split off methyl and ethyl alcohols respectively to form phenylhydantoin.

When, for instance, α -carbethoxyamino- α -phenylacetamide was warmed with dilute alcoholic potassium hydroxide, it slowly dissolved, and on diluting with water and acidifying with hydrochloric acid, an 85 per cent. yield of phenylhydantoin (m. p. 178°) was obtained. (Found, $N=15.5$. Calc., $N=15.8$ per cent.)

α -p-Methoxybenzylideneamino- α -p-methoxyphenylacetamide,
 $MeO \cdot C_6H_4 \cdot CH(N : CH \cdot C_6H_4 \cdot OMe) \cdot CO \cdot NH_2$.

A 60 per cent. yield of this substance can be obtained by treating a mixture of anisaldehyde and anisaldehydecyanohydrin with a solution of potassium hydroxide and ammonia, as previously described. The derivative, which separates after some time, recrystallises from alcohol and benzene, and melts at 141° :

0.1600 gave 0.4024 CO_2 and 0.0926 H_2O . $C=68.6$; $H=6.44$.

0.1884 „, 16.0 c.c. N_2 at 23° and 751 mm. $N=9.45$.

$C_{17}H_{18}O_3N_2$ requires $C=68.4$; $H=6.04$; $N=9.39$ per cent.

An 80 per cent. yield of the free base itself, α -amino- α -p-methoxyphenylacetamide, $MeO \cdot C_6H_4 \cdot CH(NH_2) \cdot CO \cdot NH_2$, can be obtained from this condensation product by the use of phenylhydrazine in a similar manner to that previously described in the case of the phenyl derivative.

The base is soluble in water, sparingly so in benzene, and may be recrystallised from a mixture of benzene and alcohol, from which medium it is obtained in colourless needles, melting at 134° :

0.1060 gave 14.8 c.c. N_2 at 19° and 748.5 mm. $N=15.8$.

$C_9H_{12}O_2N_2$ requires $N=15.6$ per cent.

The *benzoyl* derivative crystallises from alcohol, and melts at 184° :

0.1440 gave 13.2 c.c. N_2 at 23° and 763 mm. $N=10.4$.

$C_{16}H_{16}O_3N_2$ requires $N=9.9$ per cent.

The *carbethoxy*-derivative crystallises from hot water, and melts at 223° :

0.1560 gave 15.6 c.c. N_2 at 20° and 757.5 mm. $N=11.4$.

$C_{12}H_{16}O_4N_2$ requires $N=11.2$ per cent.

When this substance is treated with alcoholic potassium hydroxide, the solution diluted and acidified in a similar manner to that previously described, an 80 per cent. yield of *p*-methoxy-

phenylhydantoin is obtained. When crystallised from hot water, it melts at 188—189°:

0.1344 gave 16.4 c.c. N_2 at 22.5° and 749 mm. $N=13.6$.

$C_{10}H_{10}O_3N_2$ requires $N=13.6$ per cent.

The following derivatives were investigated in order to see whether it was possible to prepare six-membered rings from them. In all cases negative results were obtained.

α -Chloroacetyl-amino- α -phenylacetamide,

$C_6H_5 \cdot CH(NH \cdot CO \cdot CH_2Cl) \cdot CO \cdot NH_2$,

was obtained by the action of chloroacetyl chloride on aminophenylacetamide in benzene solution, in the presence of anhydrous sodium carbonate. The reaction takes place slowly at the temperature of the boiling solvent.

The derivative, which melts at 170°, is only sparingly soluble in benzene or ether, and may be crystallised from hot water and alcohol:

0.2340 gave 26.4 c.c. N_2 at 18° and 741 mm. $N=12.7$.

$C_{10}H_{11}O_2N_2Cl$ requires $N=12.4$ per cent.

Reaction with Diethyl Oxalate.

When the base is warmed for a short time with diethyl oxalate, a solid separates, which, when crystallised from a mixture of alcohol, water, and ethyl acetate, melts and decomposes at 195°.

The analysis given below, and the properties, showed that this was the *ethyl hydrogen oxalate* of the base,

$C_6H_5 \cdot CH(NH_2) \cdot CO \cdot NH_2 \cdot CO_2H \cdot CO_2Et$,

probably formed by the presence of a small quantity of water. It was not further investigated:

0.1456 gave 0.2854 CO_2 and 0.0870 H_2O . $C=53.5$; $H=6.6$.

$C_{12}H_{16}O_5N_2$ requires $C=53.7$; $H=6.0$ per cent.

When the base and diethyl oxalate are heated together for some time, the salt just described, which separates at first, soon dissolves. If this solution is then boiled for one hour, on cooling, a quantitative yield of *α -ethyloxalyl-amino- α -phenylacetamide,*

$C_6H_5 \cdot CH(NH \cdot CO \cdot CO_2Et) \cdot CO \cdot NH_2$,

is obtained.

It crystallises from benzene in colourless needles, melting at 116°:

0.1792 gave 17.4 c.c. N_2 at 17.5° and 765 mm. $N=11.3$.

$C_{12}H_{14}O_4N_2$ requires $N=11.2$ per cent.

When an alcoholic solution of this condensation product is treated with alcoholic potassium hydroxide, the *potassium salt* of *α -oxalyl-amino- α -phenylacetamide,*

$C_6H_5 \cdot CH(NH \cdot CO \cdot CO_2H) \cdot CO \cdot NH_2$,

separates out, and when this is decomposed by acids the free *acid* itself is obtained.

It is soluble in water or alcohol, and crystallises from ethyl acetate in colourless needles, melting and decomposing at 180° :

0.1782 gave 19.4 c.c. N_2 at 16° and 768 mm. $N=12.8$.

$C_{10}H_{10}O_4N_2$ requires $N=12.6$ per cent.

We were unable to form any six-membered cyclic derivatives from this substance or its ethyl ester; various methods usually employed for the purpose, and those which gave almost quantitative yields of hydantoins, yielded negative results in all cases.

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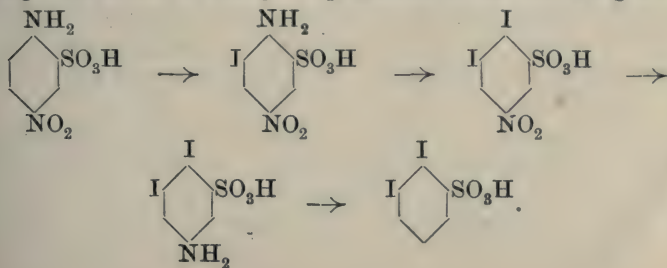
XLI.—*Iodobenzenemonosulphonic Acids. Part III.*

2:3-Di-iodo- and 2:3:4:5-tetraiodo-benzene-sulphonic Acids.

By MARY BOYLE.

Of the six theoretically possible di-iodobenzenemonosulphonic acids, four were described in 1909 (Trans., **95**, 1683); a fifth, namely, 2:3-di-iodobenzenesulphonic acid, has now been prepared and examined, and is described in the present communication.

When iodine chloride acts on a dilute hydrochloric acid solution of aniline-*o*-sulphonic acid, iodine enters exclusively into the para-position with respect to the amino-group; no trace of an ortho-isomeride can be detected. The latter substance should, however, be easily formed by first substituting the para-hydrogen atom, then introducing iodine into the free ortho-position, and finally removing the para-substituted group. Naturally, the only group that lends itself to ready introduction and elimination in this series of substances is the nitro-group, so that the first step in the synthesis of 2:3-di-iodobenzenesulphonic acid is the preparation of *p*-nitro-aniline-*o*-sulphonic acid, which substance can then be made to undergo the series of changes represented in the following scheme:



These operations proceed quite smoothly, but only moderate yields are obtained in two of the reactions; the other three give excellent results.

p-Nitroaniline-*o*-sulphonic acid was originally prepared by Fischer (*Ber.*, 1891, **24**, 3789) by heating 1-chloro-4-nitrobenzene-2-sulphonic acid with alcoholic ammonia in sealed tubes, but the difficulties and dangers in the way of this method of preparation were found to be too great to allow of its employment. It was found extremely difficult to regulate the pressure to that necessary for the displacement of the chlorine by the amino-group; explosions often occurred, and very small quantities only could be worked up at a time.

As a method by which the acid could be prepared readily and in large quantities was essential, attention was first turned to the sulphonation of *p*-nitroaniline and *p*-nitroacetanilide. The latter was subjected to the action of concentrated sulphuric acid and mixtures of concentrated and fuming sulphuric acid, at low and high temperatures, under ordinary pressure and in sealed tubes, but no sulphonation could be effected; either *p*-nitroaniline was recovered, or complete carbonisation occurred.

The nitration of aniline-*o*-sulphonic acid under varying conditions was then undertaken, and carried through successfully. By employing the acetylated derivative in the form of its barium salt and lowering the temperature considerably, a mononitro-derivative was isolated without difficulty.

The influence of temperature on the reaction is very marked, a few degrees making the difference between a good and a poor yield. For example, when the solution of the acetylated barium salt in concentrated sulphuric acid was cooled in ice, and the temperature kept at 10–15° during the addition of the requisite amount of nitric acid, the yield of nitro-acid amounted to 46.6 per cent.; when, however, the acid solution was cooled in a freezing mixture and the temperature never allowed to rise above 7°, the yield amounted to 80 per cent. of the theoretical.

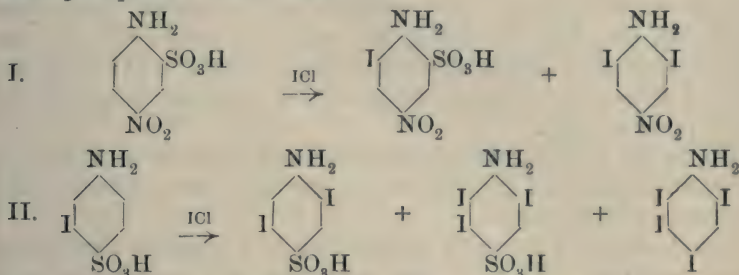
That the nitro-group displaces the hydrogen in the para-position with respect to the amino-group was proved by first displacing the latter group by iodine, then reducing the nitro-group and displacing it by iodine; in this way 2:5-di-iodobenzenesulphonic acid was obtained and identified by its appearance and the melting point of its chloride.

It is interesting to note that the isomeric acetanilide-*m*-sulphonate, which is nitrated at the ordinary temperature, 15–20°, cannot be nitrated at a temperature much below this, an attempt to improve the yield of this acid by carrying out the

operation at the low temperature essential for the formation of the *o*-nitro-isomeride proving unsuccessful.

The introduction of iodine into *p*-nitroaniline-*o*-sulphonic acid is readily brought about by the action of iodine chloride, but a secondary reaction, in which the sulphonic group is displaced by iodine, also occurs to some extent, so that a mixture of 2-iodo-4-nitroaniline-*o*-sulphonic acid and 2:6-di-iodo-4-nitroaniline is obtained. The amount of the latter substance, however, may be very considerably reduced by careful regulation of the experimental conditions.

The displacement of a sulphonic group by an iodine atom has been observed during the iodination, not only of the above nitro-substituted aniline-*o*-sulphonic acid, but also of an iodo-substituted aniline-*p*-sulphonic acid, thus:



Since the sulphur-free product occurs to a considerable extent in both cases and cannot escape detection, it is remarkable that in the earlier experiments on the iodination of the unsubstituted anilinesulphonic acids described in Part I, iodoanilines should not have been detected. In order to discover whether an tri-iodoaniline could be formed by the action of iodine chloride on aniline-*p*-sulphonic acid, an experiment was conducted in which a dilute solution of the latter was subjected to a large excess of the reagent. After concentrating the solution, the solid which separated from the cooled liquid was found to consist mainly of di-iodoaniline-sulphonic acid, together with a small quantity of a purplish-black substance free from sulphur; examination has made clear that the latter substance is not 2:4:6-tri-iodoaniline. Similarly, aniline-*o*-sulphonic acid does not yield an iodoaniline when treated with iodine chloride under ordinary experimental conditions, whilst under all conditions the sulphonic group in aniline-*m*-sulphonic acid remains unattacked.

It is clear, then, that the action of iodine chloride is comparable only to a certain extent with that of chlorine and bromine on unsubstituted amino-sulphonic acids, in which interactions the ortho- and para-isomerides yield mixtures of halogenated amino-sulphonic acids

and tri-halogen-substituted anilines, and the meta-isomeride yields halogenated aminosulphonic acids only.

Brenzinger (*Zeitsch. angew. Chem.*, 1896, **9**, 131) states that the action of bromine on the para-compound is quantitatively to displace the sulphonic group, so that the acid may be estimated by determining the sulphuric acid set free; iodine, on the other hand, only displaces the sulphonic group readily from substituted aniline-sulphonic acids, and the action does not proceed to completion.

The diazotisation of 2-iodo-4-nitroaniline-*o*-sulphonic acid proceeds smoothly, and a quantitative yield of the di-iodo-acid in the form of its potassium salt is obtained when the diazo-anhydride is decomposed with potassium iodide.

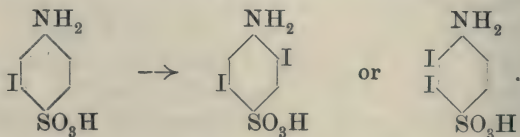
The greatest loss of material occurs during the reduction of the nitro-group, and the displacement of the amino-group by hydrogen by the diazo-reaction. Two methods of reduction have been employed, the first involving the use of ferrous hydroxide, the second that of stannous chloride in hydrochloric acid; the latter method is the more convenient, since the operation is speedy and takes place at 100°.

Up to the present, no experiments have resulted in a yield of di-iodosulphonic acid greater than 50 per cent. of the di-iodoamino-sulphonic acid employed.

The di-iodo-acid obtained in this way is a crystalline substance, which melts at 147—148°, and gives rise to a well-characterised *chloride*, melting at 127°.

An attempt has been made to prepare 2:3-di-iodobenzene-sulphonic acid in another way, and although the experiments have not been successful so far as their initial purpose is concerned, they have led to some interesting results in other directions.

When *m*-iodoaniline-*p*-sulphonic acid is subjected to the action of one molecular proportion of iodine chloride, the iodine atom introduced may occupy one of two positions, both ortho- to the amino-group; the resulting product therefore is either 2:5-di-iodoaniline-*p*-sulphonic or 2:3-di-iodoaniline-*p*-sulphonic acid:



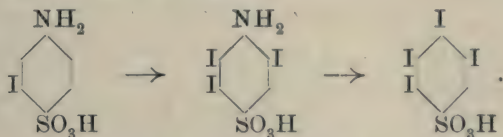
There is the third alternative that a mixture of the two acids may be produced, in which case a separation might be effected, and the 2:3-di-iodoanilinesulphonic acid converted into the desired 2:3-di-iodobenzenesulphonic acid by eliminating the amino-group.

Experimental results, however, make clear that only one position

is available for the entering iodine atom, and 2:5-di-iodoaniline-*p*-sulphonic acid is the sole product of the reaction. This fact was proved by concentrating the liquid that had been submitted to the action of the iodine chloride, collecting at intervals the crystals which separated from the cooled liquid until three or four sets of crystals had been obtained, and then displacing the amino-group in each of these by an iodine atom; each set of crystals yielded, in this way, 2:4:5-tri-iodobenzenesulphonic acid, which gave rise to a sulphonyl chloride melting sharply, even without purification, at 135°.

Confirmatory proof of the position taken up by the iodine was obtained by the production of 2:5-di-iodobenzenesulphonic acid on displacing the amino-group by hydrogen.

In some experiments the successful introduction of iodine into the second ortho-position seemed to have been achieved when a crop of more soluble crystals were found, on displacing the amino-group by iodine, to yield an iodo-sulphonic acid differing from any di- or tri-iodo-acid obtained previously. The acid, however, which is more coloured than any others and is not quite so readily soluble in water, yields a yellow chloride, melting at 163°, and proves on examination and analysis to be a tetraiodobenzenesulphonic acid, formed, without doubt, as follows:



The sparing solubility of 3-iodoaniline-*p*-sulphonic acid in water at the ordinary temperature is a difficulty in the way of preparing the tetraiodo-acid, but, as the solubility increases very considerably with temperature, and as iodine chloride undergoes no appreciable decomposition on being passed into hot aqueous solutions, the iodination may be carried out very satisfactorily at a temperature of 70—75°; under these conditions, two molecules of iodine chloride give rise to 2:3:6-tri-iodoaniline-*p*-sulphonic acid mixed with a little 2:3:4:6-tetraiodoaniline.

EXPERIMENTAL.

Preparation of p-Nitroaniline-o-sulphonic Acid.

Fifteen grams of barium acetanilide-*o*-sulphonate were dissolved in 75 grams of concentrated sulphuric acid, and cooled in ice and salt to 3°; a solution of 4.65 c.c. of concentrated nitric acid (D 1.430) in twice its volume of sulphuric acid was then added gradually, the temperature being kept at 3—7°. The addition

occupied about two hours, after which the acid liquor was allowed to remain in the mixture for another hour, and then poured into chopped ice; a clear, pale yellow liquid was obtained. This was neutralised with barium carbonate, and the clear filtrate evaporated to crystallisation, when an orange-yellow *barium* salt separated:

0.2347 gave 0.0905 BaSO_4 . $\text{Ba} = 22.68$.

$\text{C}_{12}\text{H}_{10}\text{O}_{10}\text{N}_4\text{S}_2\text{Ba}, 2\text{H}_2\text{O}$ requires $\text{Ba} = 22.76$ per cent.

The barium salt was decomposed with dilute sulphuric acid, and the acid filtrate evaporated; after concentrating to a very small bulk, the cooled liquid solidified to a mass of pale yellow needles of the nitroaminosulphonic acid, which were collected and drained on porous plate.

To prove the presence of one nitro-group only, the amino-acid was diazotised and the diazo-group displaced by iodine; the *potassium 2-iodo-4-nitrobenzenesulphonate* separated in pale yellow needles, which were purified, dried, and analysed:

0.1658 gave 5.3 c.c. N_2 at 15° and 775 mm. $\text{N} = 3.86$.

$\text{C}_6\text{H}_3\text{O}_5\text{NISK}$ requires $\text{N} = 3.82$ per cent.

2-Iodo-4-nitroaniline-o-sulphonic Acid.

Twenty grams of *p*-nitroaniline-o-sulphonic acid were dissolved in approximately 500 c.c. of water, 5 c.c. of concentrated hydrochloric acid were then added, and 15 grams of iodine chloride passed into the solution at the ordinary temperature. The yellow colour deepened to red, and a fine yellow powder gradually separated. (In some experiments under slightly different conditions, this precipitate only appeared after some time, but all experiments yielded it to some extent.) After about an hour, the solution was separated from the yellow powder and evaporated, during which operation crystals separated until further concentration was rendered impossible owing to the violent bumping. The filtrate from these crystals yielded, on almost complete evaporation, a mass of bright yellow needles of *2-iodo-4-nitroaniline-o-sulphonic acid*. The *potassium* salt crystallises in bright yellow, the *sodium* in darker yellow needles. The former was analysed:

0.1368 gave 0.0963 CO_2 and 0.0137 H_2O . $\text{C} = 19.19$; $\text{H} = 1.11$.

$\text{C}_6\text{H}_4\text{O}_5\text{N}_2\text{ISK}$ requires $\text{C} = 18.84$; $\text{H} = 1.05$ per cent.

The yellow crystals separating first were almost insoluble in water, crystallised in needles from alcohol, and were sparingly soluble in benzene. They contained nitrogen, but were devoid of sulphur, and melted at 244° . Analysis showed them to consist of

2: 6-di-iodo-4-nitroaniline, the melting point of which is given by Michael as 244° . (Found, C=18.91; H=1.11. Calc., C=18.95; H=1.05 per cent.)

In order to free 2-iodo-4-nitroaniline-*o*-sulphonic acid from the accompanying 2: 6-di-iodo-4-nitroaniline, the mixture was boiled with sodium carbonate, and the sodium salt crystallised out from the clear filtrate; this sodium salt was then dried, and used instead of the acid itself in the next operation.

Under the best conditions a yield of 71 per cent. of the iodo-nitroaminosulphonic acid was obtained—under ordinary conditions only about 53 per cent.

2: 3-Di-iodo-5-nitrobenzenesulphonic Acid.

Ten grams of sodium 2-iodo-4-nitroaniline-*o*-sulphonate were dissolved in water, and poured into excess of dilute sulphuric acid; the acid mixture was then cooled to 10° , and diazotised by the addition of 2 grams of sodium nitrite. On adding potassium iodide to the flocculent, pale yellow diazo-compound, nitrogen was at once evolved, and an aerated scum rose to the surface of the liquid; after an hour's heating on the water-bath, the precipitate was collected and purified by recrystallisation from water. It crystallises in pale yellow or cream-coloured needles, sparingly soluble in cold water.

The *potassium* salt yields an insoluble *barium* salt, from which the *acid* is obtained in silky needles by addition of sulphuric acid and subsequent concentration.

The *sodium* salt crystallises in woolly needles; the *ammonium* salt in small, pale yellow needles.

When the acid is heated in the steam-oven for a short time it becomes almost colourless, but the yellow colour is rapidly restored on exposure to moist air.

A quantitative examination of the acid and its derivatives has not yet been made.

4: 5-Di-iodoaniline-*m*-sulphonic Acid.

In one series of experiments, the nitro-group was reduced by means of ferrous hydroxide. Eight grams of the potassium salt of the nitro-acid were dissolved in about a litre of hot water, 30 grams of crystallised ferrous sulphate were added, and ferrous hydroxide was then precipitated by the addition of 15 grams of potassium hydroxide. The mixture was heated on the water-bath during four hours, after which the ferric hydroxide was separated, and the di-iodoamino-acid precipitated from the filtrate by hydro-

chloric acid. It separates in small, reddish-brown needles which are sparingly soluble in hot water.

The second method of reduction consisted in the use of stannous chloride. The finely-divided potassium salt of the nitro-acid (5 grams) was heated on the water-bath with dilute hydrochloric acid; a solution of stannous chloride in concentrated hydrochloric acid (8 grams in 20 c.c.) was then added, and the mixture was kept at 100° until the yellow nitro-acid had given place to the colourless, powdery amino-acid; the operation takes from half an hour to one hour. The amino-acid was collected, washed, and freed from insoluble matter by solution in alkali and reprecipitation with acid.

2: 3-Di-iodobenzenesulphonic Acid.

The amino-group in 4: 5-di-iodoaniline-*m*-sulphonic acid was displaced by hydrogen by boiling its diazo-anhydride with alcohol. By carrying out the diazotisation in the minimum amount of dilute sulphuric acid, it was found possible to obtain a large percentage of the diazo-salt in an insoluble condition; on boiling this diazo-salt with methylated spirit, a deep red colour was developed, and after removal of the alcohol, the sodium salt was precipitated from the aqueous solution of the residue by the addition of sodium chloride.

The *barium* salt is very sparingly soluble; on decomposition with sulphuric acid, it yields the *acid* in shining crystals, which melt at $147\text{--}148^{\circ}$.

The acid yields a well-characterised *chloride*, which separates from ether in large crystals, and melts at 127° :

0.1727 gave 0.1059 CO_2 and 0.0118 H_2O . $\text{C}=16.73$; $\text{H}=0.75$.

$\text{C}_6\text{H}_3\text{O}_2\text{ClI}_2\text{S}$ requires $\text{C}=16.80$; $\text{H}=0.70$ per cent.

Ethyl 2: 3-di-iodobenzenesulphonate separates from ether in stout needles, melting at $77\text{--}78^{\circ}$:

0.0726 gave 0.0582 CO_2 and 0.0119 H_2O . $\text{C}=21.86$; $\text{H}=1.81$.

$\text{C}_8\text{H}_8\text{O}_3\text{I}_2\text{S}$ requires $\text{C}=21.92$; $\text{H}=1.83$ per cent.

Methyl 2: 3-di-iodobenzenesulphonate separates from ether in glistening crystals, melting at 101° :

0.1313 gave 0.095 CO_2 and 0.0162 H_2O . $\text{C}=19.73$; $\text{H}=1.37$.

$\text{C}_7\text{H}_6\text{O}_3\text{I}_2\text{S}$ requires $\text{C}=19.81$; $\text{H}=1.41$ per cent.

The *sodium* salt crystallises in needles with one molecule of water of crystallisation:

0.1550 gave 0.0895 CO_2 and 0.0146 H_2O . $\text{C}=15.75$; $\text{H}=1.04$.

$\text{C}_6\text{H}_3\text{O}_3\text{I}_2\text{SNa}\cdot\text{H}_2\text{O}$ requires $\text{C}=16.00$; $\text{H}=1.11$ per cent.

The *potassium* salt separates from water in sparkling plates containing one molecule of water of crystallisation:

0.1602 gave 0.0903 CO_2 and 0.0175 H_2O . $\text{C} = 15.37$; $\text{H} = 1.21$.

$\text{C}_6\text{H}_3\text{O}_3\text{I}_2\text{SK}, \text{H}_2\text{O}$ requires $\text{C} = 15.45$; $\text{H} = 1.07$ per cent.

2: 3: 4: 5-*Tetraiodobenzenesulphonic Acid*.

m-Iodoaniline-*p*-sulphonic acid was prepared from 5-nitroaniline-*o*-sulphonic acid by the method described in the first communication on this subject (Trans., 1909, **95**, 1709). Owing to its very sparing solubility (one litre of water dissolving less than one gram at 20°), further iodination of the substance was carried out at a much higher temperature. Five grams were dissolved in about two litres of water heated to 80 — 90° , a little hydrochloric acid was added, and two molecular proportions of iodine chloride were then passed rapidly into the hot solution. There was a slight deepening of the yellow colour, and before the full amount had been passed in, a faint turbidity made its appearance. At this point the action was stopped, and the reaction mixture was kept for several hours, after which the grey powder was collected, and the clear filtrate evaporated to one-third its bulk. The crystals which separated from the cooled liquid were freed from neutral insoluble material by dissolving them in sodium carbonate solution; concentrated hydrochloric acid reprecipitated 2: 3: 6-tri-iodoaniline-*p*-sulphonic acid in greyish-white needles. The grey powder, insoluble in water and in sodium carbonate solution, did not contain sulphur, and crystallised from glacial acetic acid in small nodules, and from benzene in fine, woolly needles, melting at 163° :

0.2118 gave 0.0921 CO_2 and 0.0107 H_2O . $\text{C} = 11.85$; $\text{H} = 0.56$.

$\text{C}_6\text{H}_3\text{NI}_4$ requires $\text{C} = 12.06$; $\text{H} = 0.50$ per cent.

The substance is therefore 2: 3: 4: 6-*tetraiodoaniline*.

Sodium 2: 3: 6-tri-iodoaniline-*p*-sulphonate was then dissolved in water, poured into excess of dilute sulphuric acid, and diazotised; on decomposing the diazo-salt with potassium iodide, *potassium* 2: 3: 4: 5-*tetraiodobenzenesulphonate* separated in fine needles.

2: 3: 4: 5-*Tetraiodobenzenesulphonyl chloride* is pale yellow in colour; it crystallises from ether in small, woolly needles, melting at 161 — 162° :

0.1150 gave 0.0445 CO_2 and 0.002 H_2O . $\text{C} = 10.55$; $\text{H} = 0.19$.

$\text{C}_6\text{HO}_2\text{ClI}_4\text{S}$ requires $\text{C} = 10.58$; $\text{H} = 0.14$ per cent.

The *sodium*, *potassium*, and *ammonium* salts crystallise in small, cream-coloured needles; they are very sparingly soluble in water.

XLII.—*The Mechanism of Doebner and von Miller's Quinaldine Synthesis.*

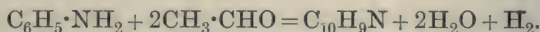
By HUMPHREY OWEN JONES and PERCY EDWIN EVANS.

DURING the examination of the case of supposed stereoisomerism, described by von Miller and Plöchl (*Ber.*, 1896, **29**, 1462), of the aldol bases, $C_{12}H_{17}ON$, derived from *m*-4-xyldine, in which it was shown (Jones and White, *Trans.*, 1910, **97**, 632) that this isomerism was structural, the change of these compounds into 2:6:8-trimethylquinoline by heat and by acids in the cold was studied. This change may be represented by the equation:



but it was found to take place without perceptible evolution of gas at temperatures above the melting point of the base and also in acid solution. The change was then carried out at 160° in an exhausted vessel connected with a Töpler pump, but even when the change was complete no gas had been produced.

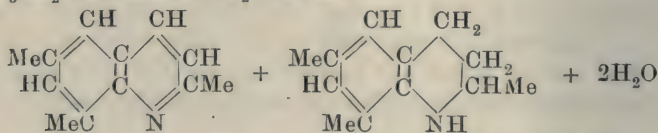
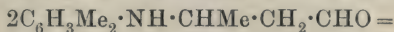
Doebner and von Miller's well-known quinaldine synthesis in presence of concentrated hydrochloric acid is usually represented by the equation:



The hydrogen in this case is found to be used in reducing some of the aldehyde, and, to a less extent, in reducing some of the quinaldine to tetrahydroquinaldine. Now the aldol bases, like many amino-aldehydes and ketones, were found not to be affected by nascent hydrogen produced from sodium and alcohol or water.

Since no hydrogen is evolved, it follows therefore either that the product formed is a derivative of dihydroquinoline, or that it consists of a mixture in equimolecular proportions of a quinoline and a tetrahydroquinoline derivative.

Experiment showed that the latter alternative was correct, and the change is represented by the equation:



either when brought about by heating to 140 — 250° or by treatment with acids.

The apparent transference of two atoms of hydrogen from one molecule to another in a quantitative manner is interesting, and

it was decided to study the reaction more fully in the hope of elucidating the mechanism by which this transference was effected.

The aldol bases are probably formed as one of the intermediate stages in Doebner and von Miller's quinaldine synthesis, and the investigation of the above change might therefore throw light on the mechanism of this important synthesis.

The present paper contains an account of the conversion of the α - and β -aldol bases, $C_{12}H_{17}ON$, obtained from *m*-4-xylidine, into 2:6:8-trimethylquinoline and 2:6:8-trimethyltetrahydroquinoline, and of the properties of these substances and of their derivatives.

The aldol base, $C_{11}H_{15}ON$, obtained from *p*-toluidine has been shown to behave similarly when heated or treated with dilute acid, yielding a mixture of 2:6-dimethylquinoline and 2:6-dimethyltetrahydroquinoline.

The aldol bases derived from aniline are not known.

It has also been found that the bimolecular ethyldenexylidine, $C_{20}H_{26}N_2$, is stable towards heat, and distils unchanged, but that when treated with acids it is very rapidly converted into a mixture in equimolecular proportions of *m*-4-xylidine, 2:6:8-trimethylquinoline, and 2:6:8-trimethyltetrahydroquinoline.

This last-mentioned reaction, if applied to the case of aniline, yields the corresponding mixture of aniline, quinaldine, and tetrahydroquinaldine.

EXPERIMENTAL.

The Action of Heat on the Aldol Bases.

The aldol bases were prepared by the method previously described (*loc. cit.*, p. 635), and it was ascertained by heating about 0.2 gram of the pure α - and β -bases in a vacuum to 160° for six hours, that less than 0.1 c.c. of gas was obtained, whereas from the equation $C_{12}H_{17}ON = C_{12}H_{13}N + H_2O + H_2$ about 24 c.c. of gas should have been evolved. The product in each case was liquid, and consisted of a mixture of a substance which reacted with benzoyl chloride and with nitrous acid and a substance which did not so react.

Similar experiments made with about 0.3 gram of the hydrochloride of the α - and β -compounds showed that no gas was evolved, although the product now gave none of the original crystalline base when neutralised.

Experiments were therefore made in which large quantities of the mixed α - and β -aldol bases were heated or treated with acid, and the resulting liquid basic product separated into its constituents, either by treatment with benzoyl chloride and alkali and washing the resulting product with acid, or by dissolving in acid and treating with dilute solution of sodium nitrite. The former method is to be preferred.

Two such experiments may be quoted as typical. 12.5 Grams of the mixed α - and β -compounds were heated to about 200° for six hours, and yielded 11.0 grams of liquid product, which, when distilled, gave 10.1 grams of a liquid boiling at 150—160°/20 mm.

From this were obtained 6.1 grams of a benzoyl derivative, corresponding with 3.8 grams of base assumed to be 2:6:8-trimethyltetrahydroquinoline and 4.9 grams of 2:6:8-trimethylquinoline. This shows that 50 per cent. of the base is 2:6:8-trimethylquinoline, and the remainder had reacted with benzoyl chloride.

An experiment with α -*d*-camphorsulphonic acid may be quoted as typical of those made with acids. In the previous paper (*loc. cit.*, p. 639) it was found, in attempting to prepare the α -*d*-camphorsulphonates of the α - and β -aldol bases in acetone solution, that these were transformed almost immediately, and the camphorsulphonate of 2:6:8-trimethylquinoline separated from the solution. This is more sparingly soluble than the camphorsulphonate of 2:6:8-trimethyltetrahydroquinoline.

11.3 Grams of the β -aldol base, dissolved in ethyl acetate, were mixed with 13.8 grams of camphorsulphonic acid, also in ethyl acetate, and the solution was evaporated. The residual mass, which crystallised on keeping and weighed 24 grams, was treated with alkali, and the two bases separated as described above. 4.9 Grams of trimethylquinoline and 7.1 grams of benzoyl derivative, corresponding with 4.5 grams of trimethyltetrahydroquinoline, were obtained, showing that the two bases were present in approximately equal quantities. The benzoyl compound obtained was found to separate from alcohol in colourless, well-formed, six-sided prisms, which melt at 143°:

0.1795 gave 0.5201 CO₂ and 0.1185 H₂O. C=81.3; H=7.55.

C₁₉H₂₁ON requires C=81.7; H=7.53 per cent.

It may therefore be concluded that the compound is 1-benzoyl-2:6:8-trimethyltetrahydroquinoline. The base recovered from the benzoyl derivative by boiling with concentrated hydrochloric acid solution and treating the acid solution with alkali was found to boil at 260—261°/780 mm. and at 142—143°/14 mm. (compare Panajotoff, *Ber.*, 1887, **20**, 34). The distillate solidified on keeping, and the crystals, which were rhombs or six-sided plates, melted at 50—51°. (Found, C=81.8; H=9.63. Calc., C=82.2; H=9.71 per cent.)

This substance was shown to be identical with that obtained by the reduction of 2:6:8-trimethylquinoline with sodium and alcohol, and is therefore 2:6:8-trimethyltetrahydroquinoline. The

same substance was recovered from the nitroso-compound by treatment with tin and hydrochloric acid.

In order to prepare larger quantities of it, the method adopted was to heat the mixture of aldol bases to 200—250° for four to six hours, to distil off the mixture of bases thus formed (this distillation may be dispensed with without affecting the result), and to reduce the whole by means of sodium and alcohol. The yield is almost quantitative.

The following derivatives of 2: 6: 8-trimethyltetrahydroquinoline have been prepared:

The *hydrochloride* separates from water in stout prisms, melting at 208—209°:

0.5001 gave 0.3320 AgCl. Cl=16.5.

$C_{12}H_{17}N, HCl$ requires Cl=16.78 per cent.

The *platinichloride* is precipitated as very minute, buff-coloured prisms on the addition of platinic chloride to a solution of the hydrochloride, and melts at 210°.

The *hydrobromide* forms colourless prisms, melting at 222—223°.

The α -d-camphorsulphonate crystallises from acetone, in which it is very soluble, in long needles, melting at 230°.

The α -d-bromocamphorsulphonate crystallises from acetone in plates, melting at 194—195°.

The *picrate* separates from a mixture of the calculated quantities of the base and picric acid dissolved in alcohol in long, bright yellow prisms, melting at 179°:

0.1773 gave 21.1 c.c. N_2 (moist) at 18° and 736 mm. N=13.5.

$C_{18}H_{20}O_7N_4$ requires N=13.9 per cent.

1-Acetyl-2: 6: 8-trimethyltetrahydroquinoline crystallises from alcohol in colourless, micro-crystalline needles, melting at 108—109°.

1: 2: 6: 8-Tetramethyltetrahydroquinoline hydriodide was formed as a solid, crystalline mass from a mixture of methyl iodide and 2: 6: 8-trimethyltetrahydroquinoline in molecular proportions. It separates from hot alcoholic solution in stellate aggregates of colourless prisms, which melt at 168—169°:

0.2645 gave 0.4760 CO_2 and 0.1500 H_2O . C=49.0; H=6.2.

$C_{13}H_{20}NI$ requires C=49.2; H=6.31 per cent.

1: 2: 6: 8-Tetramethyltetrahydroquinoline separates from the above salt on treatment with alkali as an almost colourless oil, boiling at 256—257°/775 mm.:

0.2835 gave 0.8540 CO_2 and 0.2545 H_2O . C=82.2; H=9.96.

$C_{13}H_{19}N$ requires C=82.5; H=10.0 per cent.

The *picrate* of the base separates from alcohol in long, lustrous, yellow prisms, melting at 190—191°.

The *platinichloride* is precipitated as buff-coloured needles on the addition of platinic chloride to a solution of the base in hydrochloric acid; it melts and decomposes at 205°.

1-Benzyl-2:6:8-trimethyltetrahydroquinoline hydriodide is deposited slowly from a mixture of benzyl iodide and 2:6:8-trimethyltetrahydroquinoline. It separates from alcohol in long needles, melting and decomposing at 227°:

0.1901 gave 0.1130 AgI. $I = 31.8$.

$C_{19}H_{24}NI$ requires $I = 33.3$ per cent.

The available information concerning 2:6:8-trimethylquinoline (Panajotoff, *loc. cit.*) is scanty, so the following additional facts are recorded here.

The base itself crystallises readily in rhombs or diamond-shaped plates, melting at 45—46°, and boiling at 266—267°/780 mm. (Panajotoff gives 260°/719 mm.).

The hydrochloride and *hydrobromide* form colourless prisms, melting at 207° and 172—173° respectively.

The *hydriodide* crystallises in stout, yellow prisms, melting at 223—224°.

The *platinichloride* is a buff-coloured, micro-crystalline powder, melting at 206—207°.

The *picrate* forms bright yellow prisms, melting at 187—189°.

The *α-d-camphorsulphonate* melts at 231—232°.

It has also been shown that the corresponding aldol bases formed from *p*-toluidine and acetaldehyde in acid solution (*loc. cit.*, p. 643) are transformed, on heating alone or on treatment with acids, into a mixture of 2:6-dimethylquinoline (*p*-toluquinaldine) and 2:6-dimethyltetrahydroquinoline in equimolecular proportions.

It has been found that the bimolecular ethyldenexylidine, $(C_{10}H_{13}N)_2$, which can be produced from the aldol bases and *m*-4-xylidine; or from the latter and acetaldehyde in alcohol solution (*loc. cit.*, p. 640), when treated with acids, is very rapidly transformed into a mixture of the salts of xylidine, 2:6:8-trimethylquinoline, and 2:6:8-trimethyltetrahydroquinoline; xylidine can be separated from the quinoline derivatives by distillation, and the two last are then separated as described above. The aldol bases from aniline have not been prepared, but this modification allows of the synthesis of 2-methylquinoline (quinaldine) and its tetrahydro-derivative from aniline by the following process.

One hundred grams of aniline are treated at 0° with 50 c.c. of commercial "concentrated" acetaldehyde with continual stirring, the resulting viscous mass is at once dissolved in about 800 c.c. of hydrochloric acid (about 5*N*), and heated to 100° for an hour. The solution is rendered alkaline, and the bases are separated and

distilled. Fifty grams of aniline are recovered, and about 25 grams of a mixture of bases, boiling at 235—255°, are obtained. This mixture was separated by benzoylating and removal of the 2-methylquinoline by means of acid, and in two experiments 4·8 and 4·9 grams of 2-methylquinoline were obtained from 10 grams of the mixture. The benzoyl derivative of 2-methyltetrahydroquinoline, melting at 119—120°, was also isolated, thus showing that 2-methylquinoline and its tetra-hydro-derivative had been produced in equimolecular quantities.

Commercial "quinaldine" always contains some of the tetrahydro-derivative, and a specimen obtained from the Actien Gesellschaft für Anilin-Fabrikation was found to contain about 14 to 16 per cent.

The expenses of this work were partly defrayed by means of grants received from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

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XLIII.—*Experiments on the Formation of 4(or 5)- β -Aminoethylglyoxaline from Histidine.*

By ARTHUR JAMES EWINS and FRANK LEE PYMAN.

4(or 5)- β -AMINOETHYLGLYOXALINE, the base derived from the naturally occurring amino-acid histidine (α -amino- β -glyoxaline-4(or 5)-propionic acid) by the removal of carbon dioxide from the latter has recently become of considerable interest and importance on account of its occurrence in extracts of ergot (Barger and Dale, *Trans.*, 1910, **97**, 2592) and very great physiological activity (Dale and Laidlaw, *J. Physiol.*, 1910, **41**, 318). It has hitherto been obtained by two methods: (1) by synthesis; (2) by the action of putrefactive organisms on histidine itself.

The base was first synthesised by Windaus and Vogt (*Ber.*, 1907, **40**, 3691) from β -glyoxaline-4(or 5)-propionic acid by Curtius's method. More recently, Ackermann (*Zeitsch. physiol. Chem.*, 1910, **65**, 504) has succeeded in obtaining a relatively large yield of the base by the putrefaction of histidine.

Neither method is very satisfactory, since the first is somewhat complex and expensive, while the yields are by no means good. The second method is wholly uncertain in its results. The object

of our investigation was therefore to endeavour to find a simple method of obtaining the base directly from histidine, which is comparatively easily obtainable. In this we were only partly successful, since we were able to obtain only moderate yields of the base by the action of acids in sealed tubes at a temperature of from 265° to 270° . This last factor (temperature) made it a matter of very great difficulty to obtain anything like large amounts of the base. The results obtained, however, were deemed of sufficient interest to form the subject of the present communication.

Experiments were first carried out to determine whether, as in the case of the formation of *p*-hydroxyphenylethylamine from tyrosine, carbon dioxide could be removed from histidine by direct heating. It was found, however, that under varying conditions only a very small amount (0.3 to 1.0 per cent.) of base could be obtained, and the method was abandoned.

By directly heating the monobenzoyl derivative of histidine and subsequently hydrolysing, a somewhat better yield (10 to 20 per cent.) of the base was obtained.

The effect of various acids under varying conditions of temperature and concentration was then investigated, and it was found that yields of base amounting to about 25 per cent. of the theoretical could be obtained with concentrated hydrochloric acid, moderately dilute sulphuric acid, and fused potassium hydrogen sulphate under suitable conditions. After heating for three hours with acids at temperatures below 240° , no formation of 4(or 5)- β -aminoethylglyoxaline took place. At about 240° very little of the base was obtained, the main product of the reaction being *r*-histidine, which had previously been prepared by Fränkel (*Beitr. Chem. Physiol. Path.*, 1906, **8**, 156) in a similar manner. As the temperature was raised, the yield of base gradually improved, and reached a maximum (about 25 per cent. of the theoretical) at about 265 — 270° . Further increase of temperature led to diminished yield of 4(or 5)- β -aminoethylglyoxaline. With phosphoric acid (44 per cent.) at 250° , no base was produced, nor did the use of hydrogen bromide in acetic acid solution at somewhat lower temperatures yield any better results.

The progress of the work was very greatly facilitated by the physiological estimation of the yield of base in many of our experiments. This was kindly undertaken for us by Dr. H. H. Dale and Dr. P. P. Laidlaw, to whom we wish to express our indebtedness and thanks.

During the course of the investigation some hitherto undescribed salts of histidine and 4(or 5)- β -aminoethylglyoxaline were prepared, and are now described.

EXPERIMENTAL.

The Action of Concentrated Hydrochloric Acid on Histidine.

One gram of histidine hydrochloride was heated in a sealed tube with 2 c.c. of concentrated hydrochloric acid to 270° for three hours. The solution was concentrated and neutralised. To the boiling solution was added an excess of solid picric acid. On cooling, a crystalline precipitate separated, which was collected and freed from picric acid by extraction with ether. The residue, when recrystallised from water, gave 0.2 gram of 4(or 5)- β -aminoethylglyoxaline dipicrate, melting at $233\text{--}235^{\circ}$.

The Action of Dilute Sulphuric Acid.

(a) At $265\text{--}270^{\circ}$.—Two grams of histidine monohydrochloride were heated in a sealed tube to $265\text{--}270^{\circ}$ for three hours with 4 c.c. of a 20 per cent. aqueous solution of sulphuric acid. The reaction product (a dark brown liquid) was treated with sodium carbonate solution until no further precipitate separated, filtered, and the filtrate neutralised and concentrated to about 15 c.c. An equal volume of cold saturated aqueous solution of picric acid was added, and the amorphous precipitate quickly collected. To the filtrate was added 1.5 grams of picric acid in hot saturated aqueous solution. A little resinous precipitate was removed from the hot solution, and the crystalline precipitate, which separated on cooling, was recrystallised from hot water. There was thus obtained 0.85 gram of a picrate (m. p. $228\text{--}229^{\circ}$), which crystallised in bunched, slightly curved, pointed needles. Repeated recrystallisation did not raise the melting point above $233\text{--}234^{\circ}$, and analysis showed the salt to be the hitherto undescribed 4(or 5)- β -aminoethylglyoxaline monopicate:

0.0978 gave 0.1396 CO_2 and 0.0282 H_2O . $\text{C}=38.8$; $\text{H}=3.2$.

$\text{C}_{11}\text{H}_{12}\text{O}_7\text{N}_6$ requires $\text{C}=38.8$; $\text{H}=3.5$ per cent.

The monopicate, on recrystallisation from a large excess of picric acid solution, readily yielded the dipicrate corresponding in all respects with that described by Windaus and Vogt (*loc. cit.*).

4(or 5)- β -Aminoethylglyoxaline Dihydrobromide.

The dihydrobromide was prepared by thoroughly shaking the finely powdered dipicrate with ether and a slight excess of dilute hydrobromic acid until all the dipicrate had disappeared. The aqueous solution of the hydrobromide thus obtained was then freed from picric acid by means of ether, digested with a little animal charcoal, filtered, and evaporated to dryness in a vacuum. The

residual brown gum became crystalline on the addition of absolute alcohol, and the salt was then purified by recrystallisation from this solvent.

The salt forms stout, colourless, prismatic needles, which melt to a brown liquid at 284° (corr.), after gradually darkening and sintering from about 265° . It is very readily soluble in water, but sparingly so in boiling absolute alcohol. It is anhydrous:

0.1200 gave 0.0957 CO_2 and 0.0440 H_2O . $\text{C}=21.7$; $\text{H}=4.1$.

$\text{C}_5\text{H}_9\text{N}_3, 2\text{HBr}$ requires $\text{C}=22.0$; $\text{H}=4.1$ per cent.

(b) At $240\text{--}250^{\circ}$.—Seventy grams of histidine monohydrochloride were heated in sealed tubes with 140 c.c. of 20 per cent. sulphuric acid for three hours at $240\text{--}250^{\circ}$ in quantities of not more than 4 grams of histidine in one tube; even under these conditions tubes representing 23 grams exploded. The reaction product from the remaining tubes was worked up exactly as described above. There was thus obtained 26.7 grams of a picrate, which melted at $180\text{--}190^{\circ}$. On extracting with absolute alcohol, the greater portion dissolved, and the sparingly soluble residue, after recrystallisation from water, gave 4.3 grams of 4(or 5)- β -aminoethylglyoxaline dipicrate. The alcoholic extract was evaporated, and the residue, on crystallisation from water, gave 16.6 grams of pure *r*-histidine dipicrate

r-Histidine dipicrate crystallises from water in thin, yellow plates, which contain two molecules of water. After drying at 100° , it begins to sinter at 182° , and decomposes at 190° (corr.). It is readily soluble in alcohol or hot water, but sparingly so in cold water:

0.1660 * lost 0.0091 at 100° . $\text{H}_2\text{O}=5.5$.

$\text{C}_{18}\text{H}_{15}\text{O}_{16}\text{N}_9, 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=5.5$ per cent.

0.1468 † gave 0.1906 CO_2 and 0.0356 H_2O . $\text{C}=35.4$; $\text{H}=2.7$.

0.1364 † „ 24.0 c.c. N_2 at 23° and 766 mm. $\text{N}=20.5$.

$\text{C}_{18}\text{H}_{15}\text{O}_{16}\text{N}_9$ requires $\text{C}=35.2$; $\text{H}=2.5$; $\text{N}=20.6$ per cent.

This salt readily gave the dihydrochloride, which sinters and melts at 225° (corr.): Fränkel (*loc cit.*) gives 220° .

r-Histidine sesquihydrochloride, $(\text{C}_6\text{H}_9\text{O}_2\text{N}_3)_2, 3\text{HCl}, \text{H}_2\text{O}$, crystallises in clusters of flat, prismatic needles when the dihydrochloride is crystallised from dilute alcohol (for instance, when it is dissolved in about twice its weight of water, and four times its weight of alcohol is added). This salt melts at $168\text{--}170^{\circ}$ (corr.), and suffers no loss in weight at 100° :

0.1513 gave 0.1840 CO_2 and 0.0734 H_2O . $\text{C}=33.2$; $\text{H}=5.4$

0.1270 „ 0.1530 CO_2 „ 0.0644 H_2O . $\text{C}=32.9$; $\text{H}=5.7$.

* Air-dried salt.

† Dried at 100° .

0.1570 gave 0.1555 AgCl. Cl=24.5.

0.1259 „ 0.1251 AgCl. Cl=24.6.

(C₆H₉O₂N₃)₂.3HCl.H₂O requires C=32.9; H=5.3;
Cl=24.3 per cent.

The composition of this salt is peculiar; there is no evidence of a similar salt of the natural histidine (compare Abderhalden and Einbeck, *Zeitsch. physiol. Chem.*, 1909, **62**, 322).

r-Histidine monopicrate crystallises from water in large, flat plates, which are sparingly soluble in hot water and almost insoluble in alcohol. This salt decomposes at 180—181° (corr.), after sintering from about 175°. It contains one molecule of water of crystallisation:

0.3983 * lost 0.0185 at 110°. H₂O=4.6

C₁₂H₁₂O₉N₆.H₂O requires H₂O=4.5 per cent.

0.1825 † gave 0.2515 CO₂ and 0.0531 H₂O. C=37.6; H=3.3.

C₁₂H₁₂O₉N₆ requires C=37.5; H=3.2 per cent.

When this salt is dissolved in a hot aqueous solution of picric acid, the dipicrate (m. p. 190°) separates on cooling.

For purposes of comparison, attempts were made to prepare a mono- and di-picrate of naturally occurring histidine. Histidine appears, however, to form only a dipicrate.

Histidine dipicrate crystallises from water in long, flat, clear, well-formed leaflets, which sinter at about 80° and melt at 86° (corr.). It appears to contain two molecules of water:

0.1591 * gave 0.1927 CO₂ and 0.0452 H₂O. C=33.0; H=3.2.

C₁₈H₁₅O₁₆N₉.2H₂O requires C=33.3; H=3.0 per cent.

The Action of Potassium Hydrogen Sulphate on Histidine.

Twenty-five grams of potassium hydrogen sulphate were fused in a beaker heated by an oil-bath and 1 gram of histidine monohydrochloride was added; considerable frothing occurred, and the mixture had to be stirred frequently. After heating for various lengths of time at different temperatures, the reaction product was dissolved in water, neutralised with potassium hydroxide, digested with animal charcoal, cooled, and filtered from charcoal and potassium sulphate. The filtrate was again concentrated, separated from more potassium sulphate, made up to a known volume, and the yield of 4(or 5)- β -aminoethylglyoxaline determined physiologically. Heating at an oil-bath temperature of 260—270° for one hour gave the best yield of the desired base, but the maximum only reached about 5 per cent. of the theoretical. A modification of this method, in which histidine monohydrochloride was heated with ten times its

* Air-dried salt.

† Dried at 110°.

weight of potassium hydrogen sulphate in sealed tubes at 265—270° for three hours, gave yields of 20 to 25 per cent. of the theoretical, as indicated by physiological estimation.

The Formation of 4(or 5)- β -Aminoethylglyoxaline from Benzoyl-histidine.

Monobenzoylhistidine was prepared by the Schotten-Baumann method, as indicated by Fränkel (*loc. cit.*). It was, however, found to be quite unnecessary to carry out the precipitation with mercuric chloride described by him. On neutralising the solution after the reaction is complete, the pure benzoyl derivative separates very quickly on simply keeping.

One gram of benzoylhistidine so obtained was heated in a vacuum at 240° until all frothing ceased. The black, tarry mass was dissolved in 2 c.c. of concentrated hydrochloric acid, and hydrolysed at 180°. The contents of the tube were washed out with water, and the separated benzoic acid collected, the filtrate extracted with ether, and the aqueous solution neutralised. An equal volume of a solution of picrolonic acid in water was added, and the bulky, amorphous, yellow precipitate collected. The filtrate was concentrated to small bulk, and a concentrated alcoholic solution of picrolonic acid added. After some time, 0.47 gram of 4(or 5)- β -aminoethylglyoxaline picrolonate was obtained, crystallising in bunched needles, and melting at 262—264° (Windaus and Vogt, *loc. cit.*, give "about 266°").

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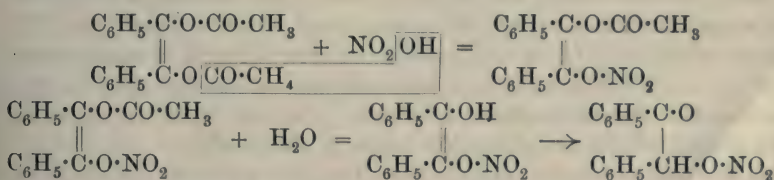
XLIV.—*The Nitration of Acetylbenzoin and of Stilbenediol Diacetates.*

By ARTHUR GORDON FRANCIS and CHARLES ALEXANDER KEANE.

THE object of this investigation has been to obtain some unsymmetrical derivatives of benzoin, such as the nitro-compounds, with the view of examining their stereochemical and desmotropic relations. The action of nitric acid on benzoin and some allied compounds offers several points of interest. Benzoin itself, as is well known, is oxidised to benzil when heated with ordinary concentrated nitric acid, but with fuming nitric acid at 0° *p*-nitrobenzil is also obtained.

Benzil is less readily nitrated; on heating it with fuming nitric acid, two nitro-groups are introduced to form two isomeric dinitro-compounds, melting respectively at 131° and 147° (Zagumenny, *J. Russ. Phys. Chem. Soc.*, 1873, **4**, 278); mononitrobenzils have not been obtained directly from benzil. The action of nitric acid on acetyl- and on benzoyl-benzoin has been studied by Zinin (*Annalen*, 1857, **104**, 116). From acetylbenzoin he obtained a mixture of two nitro-compounds, neither of which, however, appears to have been isolated in a pure state or submitted to more than a preliminary investigation. The nitrobenzoyl compound he obtained pure, and isolated it in rhombic tablets, melting at 137° .

With the object of preparing nitrobenzoin, attempts were first made to hydrolyse nitrobenzoylbenzoin, but it was not found possible to effect this decomposition with any hydrolytic agents, as complex condensation products, which are still under investigation, invariably resulted. In order to obtain a less stable ester, *p*-nitroacetylbenzoin was prepared, but condensation products were similarly formed on hydrolysis, and all attempts to obtain *p*-nitrobenzoin by the action of hydrolytic agents from it were unsuccessful. Attention was then directed to the nitration of the geometrically isomeric stilbenediol diacetates prepared by Thiele (*Annalen*, 1899, **306**, 142). These compounds are so readily hydrolysed to benzoin that it appeared probable that by effecting the nitration in absence of hydrolytic agents, nitro-compounds of the diacetyl isomerides might be obtained, from which nitrobenzoin could be prepared. The experiments conducted with this object in view resulted in the formation of benzoin mononitrate and a small quantity of a substance, possibly nitrobenzoin, which is still under examination, together with benzil. Both the α -stilbenediol diacetate melting at 153° and the β -compound melting at 110° act similarly towards nitric acid, except for the fact that the isomeride of lower melting point is partly converted into the α -compound under the conditions described below. The action of nitric acid may be represented by the following equations, the final formation of benzoin nitrate being due to a molecular rearrangement, as in the preparation of benzoin from the stilbenediol diacetates:



This difference in the behaviour of acetylbenzoin, benzoylbenzoin,

and of the stilbenediol diacetates towards nitric acid is shared by several other reagents, and similar differences have also been observed with some of their derivatives. These reactions are under further investigation.

EXPERIMENTAL.

Nitration of Acetylbenzoin.

Zinin (*Annalen*, 1857, **104**, 120), Jena and Limpricht (*ibid.*, 1870, **155**, 92), and Pöpcke (*Ber.*, 1888, **21**, 1336) have all prepared acetylbenzoin, but give different melting points for the compound, namely, below 100° , 75° , and 83° respectively. It is best prepared as follows: 200 grams of benzoin are added in successive small quantities to a mixture of 25 c.c. of concentrated sulphuric acid and 500 c.c. of acetic anhydride kept cold in running water; the mixture is kept for some time, poured into water, the precipitate collected, and recrystallised from 90 per cent. alcohol. The product thus prepared melts at 83° , agreeing with the value given by Pöpcke. A practically quantitative yield is obtained by this method of preparation.

Two methods of nitration were employed.

Method I.—For the nitration by this method, 400 grams of fuming nitric acid are cooled to 0° in a freezing mixture of ice and salt, and 200 grams of finely powdered acetylbenzoin gradually added. The acetyl compound must be thoroughly dry, free from odour of acetic acid, and finely powdered, and the temperature must be kept within a degree or so of 0° ; if it falls much below this temperature, considerable quantities of benzoin are formed, and above this temperature the amount of benzil formed is increased. The deep red solution thus obtained is poured at once into ice-cold water, when a pale green oil separates, which is well washed by decantation with water. After some time this sets to a semi-solid mass, from which the nitro-compound is separated by treatment with successive small quantities of ether, whereby the adherent oil is removed. The residue is recrystallised from 90 per cent. alcohol. A yield of 20 per cent. on the weight of acetylbenzoin taken is obtained.

Method II.—Five grams of acetylbenzoin are treated with 25 c.c. of acetic anhydride, 4 c.c. of concentrated sulphuric acid, and 1.7 grams of recently fused and finely powdered nitre at a temperature of -15° . The nitration is carried out as in the case of the stilbenediol diacetates described below. A yield of 40 per cent. on the weight of the acetylbenzoin taken is obtained.

p-Nitroacetylbenzoin crystallises from 90 per cent. alcohol in brilliant, almost colourless leaflets, and melts at 125° (uncorr.). It

is sparingly soluble in ether or light petroleum, readily so in chloroform, acetone, or benzene, and somewhat less so in boiling 90 per cent. alcohol or glacial acetic acid. It is decomposed by alkalis in either aqueous or alcoholic solution, with the formation of acidic condensation products, as stated above:

0.2064 gave 0.4846 CO_2 and 0.0834 H_2O . $\text{C}=64.03$; $\text{H}=4.48$.

0.5640 „, 24.0 c.c. N_2 (moist) at 20° and 755 mm. $\text{N}=4.83$.

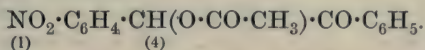
0.7421, in 20 c.c. alcohol, gave $\text{E}=0.19^\circ$. $\text{M.W.}=305$.

$\text{C}_{16}\text{H}_{13}\text{O}_5\text{N}$ requires $\text{C}=64.20$; $\text{H}=4.35$; $\text{N}=4.68$ per cent.

$\text{M.W.}=299$.

When heated with nitric acid ($\text{D } 1.40$), *p*-nitrobenzil, melting at 140° , is formed. (Found, $\text{N}=5.34$. Calc., $\text{N}=5.49$ per cent.)

When oxidised with a mixture of sulphuric acid (25 grams of concentrated sulphuric acid in 25 c.c. of water) and an approximately normal solution of potassium dichromate, it is completely hydrolysed and oxidised to acetic acid, benzoic acid (melting at 122°), and *p*-nitrobenzoic acid (melting at 237°). Care must be taken to have always an excess of dichromate present during the oxidation, otherwise acidic condensation products result. Benzoïn, under precisely the same conditions, yields molecular proportions of benzaldehyde and benzoic acid. From this it follows that the nitro-group is in the para-position in the phenyl radicle connected with the carbon atom of the secondary alcohol group, so that the nitroacetylbenzoïn has the structural formula:



The identity of the *p*-nitrobenzoic acid formed in the oxidation was confirmed by titration with alkali. (Found, $\text{M.W.}=166.4$. Calc., $\text{M.W.}=167$.)

Nitration of the Stilbenediol Diacetates (α , melting at 153° , and β , melting at 110°).

Forty c.c. of concentrated sulphuric acid are added, drop by drop, to 250 c.c. of acetic anhydride kept cold in a freezing mixture of ice and salt; when the temperature has fallen to -15° , 45 grams of the finely powdered β -stilbenediol diacetate (melting at 110°) are added, and then 17 grams of recently fused and finely powdered nitre in small portions at a time and with constant shaking, care being taken to keep the temperature at -15° . If the diacetate be added to the mixed acid, anhydride, and nitre, no benzoïn nitrate is formed. When all the nitre has been added, the solution, which is clear and red in colour, is poured into the bath liquor, cooled to -15° , and the whole stirred until solid. The supernatant acid liquid is then decanted, the residue being thoroughly washed by

decantation, and collected. The bulk of the benzil present is removed by washing with ether, and the residue purified by fractional crystallisation from 90 per cent. alcohol. The products isolated consisted of: (1) benzoin mononitrate, melting at 167° , 3 grams; α -stilbenediol diacetate, melting at 153° , 3 grams; and the substance, melting at 188° , 1 gram.

The amount of α -stilbenediol diacetate formed increases with decrease of temperature; at 0° , 5 per cent. of the β -diacetate used is obtained, at -15° , 7 per cent., at -25° , 10 per cent., whilst no benzoin nitrate is formed either at 0° or at -25° .

The α -diacetate, melting at 153° , gives a somewhat better yield of benzoin nitrate, 25 grams yielding 2 grams of benzoin nitrate, melting at 167° , and 2 grams of unchanged α -diacetate, melting at 153° . None of the β -isomeride is formed in the reaction.

Benzoin mononitrate crystallises from 90 per cent. alcohol in beautiful, colourless plates, and melts at 167° (uncorr.). It is very sparingly soluble in ether, light petroleum, or cold 90 per cent. alcohol, but dissolves fairly readily in boiling 90 per cent. alcohol. On hydrolysis with potassium hydroxide, it yields benzoin and potassium nitrate, and on heating with concentrated nitric acid it gives benzil. The complete combustion of the nitrate is exceedingly difficult, as it burns explosively; the analytical results, however, leave no doubt as to the composition of the compound:

0.1461 gave 0.3482 CO_2 and 0.0732 H_2O . $\text{C}=65.0$; $\text{H}=5.56$.

0.1891 „ 8.70 c.c. N_2 (moist) at 15° and 762 mm. $\text{N}=5.41$.

0.2090 „ 9.25 c.c. N_2 „ „ 14° „ 763 mm. $\text{N}=5.23$.

0.4838, in 20 c.c. alcohol, gave $\text{E}=0.16^{\circ}$. $\text{M.W.}=238$.

$\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}$ requires $\text{C}=65.37$; $\text{H}=4.28$; $\text{N}=5.45$ per cent.

$\text{M.W.}=257$.

The substance melting at 188° is very sparingly soluble in 90 per cent. alcohol, but can be obtained crystalline from this solvent in fine, light yellow needles. It is unchanged by boiling with potassium hydroxide, and is therefore not a nitrate; its composition corresponds with that of nitrobenzoin:

0.3482 gave 16.4 c.c. N_2 (moist) at 13° and 760 mm. $\text{N}=5.57$.

$\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}$ requires $\text{N}=5.45$ per cent.

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XLV.—*Studies of the Processes Operative in Solutions.*
Part XII. The Apparent Hydration Values of*
the Acid Systems and of Salts deduced from a
Study of the Hydrolytic Activities of Acids.

By FREDERICK PALLISER WORLEY, M.A., M.Sc., New Zealand,
 Leathersellers' Company's Research Fellow, City and Guilds of
 London Institute, Central Technical College.

THE first communication of this series was an account of experiments made with the object of studying the influence of various "neutral" substances, both electrolytes and non-electrolytes, on the sucroclastic activity of chlorhydric acid; in the third, similar experiments with nitric acid were described; in the seventh, the relative activities of the two acids and of sulphuric acid were compared from several points of view; in the eighth, the nature of the influence on the hydrolytic activity of acids exercised by salts was considered more broadly than in previous communications, especially with reference to the peculiarities apparent in the case of weak hydrolytes.

The present communication is an account of a closer and more complete study of the behaviour of cane sugar in aqueous solutions towards chlorhydric and nitric acids and of the influence of salts on the rate of change than was possible heretofore with the appliances at disposal; although undertaken with the object of obtaining the data for a full discussion of the processes operative in hydrolytic changes, it has afforded results that render the careful consideration desirable of the extent to which the polarimetric method may be used as a method of following the course of a chemical change. It was felt that the experimental difficulties attending such an inquiry had not all been overcome—particularly that it was necessary to secure more complete control over the

* The previous parts of these studies (I—XI) are published in the Proceedings of the Royal Society, A, 1906, **78**; 1907, **79**; 1908, **81**; 1910, **84**. A summary of the work is given in No. XIX. (*Chem. News*, 1911, **103**, 97). Attention may be called to certain departures from the conventional nomenclature adopted in the communications. The compound represented by the formula HCl is termed hydrogen chloride, not hydrochloric acid, for reasons advocated by me as far back as 1885 in my address to the Chemical Section of the British Association in Aberdeen; the acid that is formed when hydrogen chloride and water associate is spoken of as chlorhydric acid. In like manner, the compound formulated as $\text{HO}\cdot\text{NO}_2$ is spoken of as hydric nitrate, the solution of this compound in water being alone spoken of as nitric acid. The object in view in adopting this course will be discussed in a later communication.—HENRY E. ARMSTRONG.

temperature conditions—and that if the refinements of which an account has been given previously (IX) were introduced the errors would at least be reduced to a minimum, so that it would be possible, with a close approach to certainty, to determine the direction in which departures from constancy took place as the action progressed or when the conditions were varied.

In previous work, cane sugar has been used as the hydrolyte in order to ascertain the effect produced by various substances on the course of change; the inquiry was undertaken in the hope that evidence would be obtained as to the state of the substances in solution.

The changes undergone by the sugar and their possible influence on the course of change have scarcely been taken into consideration hitherto. It has always been assumed tacitly that the resolution of the sugar molecule into the two hexose molecules is without influence on the result but it is difficult to believe that this is the case, as the increase in the number of molecules in solution must affect the "osmotic" conditions and must give rise to disturbances of some magnitude: if such changes be not apparent in the result, it must be because compensating influences are at work which mask their effect.

Again it is customary to suppose that it is unnecessary to take into account the water which disappears as hydrolysis proceeds—on the ground that this forms only a small proportion of the total amount present; it appeared to be desirable to ascertain the limits within which this argument held good and within which the observations might be reduced on the assumption that only a single changing substance is to be considered.

Determination of the End-point in the case of Concentrated Solutions.

It has been customary to follow the course of change with the polarimeter, observing the rotatory power of the solution at known intervals of time, a final observation being made to determine the "end-point" when the change is judged to be complete. This determination is of primary importance: if the end-point be determined incorrectly, it is impossible to deduce a correct value of K in the mass-action equation:

$$K = \frac{1}{t} \log \frac{a}{a-x}.$$

At an early stage of the inquiry, doubt arose as to the propriety of the method usually adopted. When observations were carried on during a considerable period, the disquieting fact was disclosed that

the action did not come to an end. Thus, in an experiment with one molecular proportion of cane sugar, one of hydrogen chloride and forty of water, the solutions were mixed at 10.35 a.m. on a Friday and readings were taken at intervals until 9.15 a.m. on the following day: by four o'clock on Friday afternoon, the rotatory power had fallen to 161.34° (the zero being approximately 180°); at five o'clock it was 161.22° ; from six until eight it was constant at 161.20° ; it then began to rise, the readings being 161.21° at 9 p.m., 161.25° at 12.30 a.m., 161.28° at 3 a.m., 161.30° at 6.30 a.m., 161.335° at 9.15 a.m. Under the usual conditions, the final reading would not have been taken probably until several hours later, when the rotatory power would have risen still further.

Even in the case of much more dilute solutions, the rise is easily detected. In an experiment made with only a quarter as much sugar as in that above quoted, the solutions were mixed at 10.20 a.m. on Friday: at 2.30 p.m. the reading was 174.86° , at 3.30 p.m. 174.66° , at 5.30 p.m. and at 6.10 p.m. it lay between 174.65° and 174.66° ; by noon the next day, it had risen to 174.67° and by 3.45 p.m. on Monday to 174.74° .

Although, in the case of dilute solutions, the change in the "end-point" is often so small as to be negligible, in the case of relatively concentrated solutions it cannot be neglected. Apparently the rise is due to a change affecting one or both of the primary products of hydrolysis. It is to be supposed that this change sets in as soon as the hydrolysis begins and that it continues at an increasing rate as the hexoses increase in amount, reaching a maximum towards the close of the period of hydrolysis.

The apparently constant minimum is reached when the change in the rotatory power due to the hydrolysis becomes as small as that due to the secondary change; it is not the minimum that would have been obtained in the absence of secondary change but a higher value. Moreover, when the end-point is deduced in the usual way from a single observation about twenty-four hours from the commencement of the experiment, probably the minimum has been passed and the rotatory power has increased, thus introducing a still greater error.

The question arises whether this change (which sets in at the beginning of the experiment) affects readings other than those of the end-point? In point of fact, there can be little doubt that its effect is so small at the beginning of the hydrolysis as to be negligible. To determine the rate at which the primary change occurs, however, it is necessary to eliminate the effect of the secondary change by finding the end-point that would have been reached if the primary change alone had occurred.

It is impossible to deduce a "theoretical" end-point, both on account of the effect of the catalyst on the rotatory power of the cane sugar and of the hexoses into which it is converted and on account of the effect that the various optically active substances exercise reciprocally on their individual rotatory powers. The preparation of solutions containing the two hexoses and the acid catalyst with the required amount of water such as should remain at the close of the experiments, if not out of the question, would be difficult on account of the trouble and errors involved in this procedure.

Fortunately it is possible to correct for the secondary change in each experiment by determining the rate at which the change is taking place. For this purpose, after the rise becomes regular, readings are taken at intervals of from eight to twenty-four hours. The total effect of the secondary change is then found by assuming that it has continued at this rate from the time when half the sugar has been inverted. It is believed that this method affords a very close approximation to the truth. The result is most conveniently arrived at graphically.

By proceeding in this manner, the "corrected" end-point deduced in the case of the example quoted was 161.11° , whereas that observed directly in the ordinary way would have been about 161.4° .

Evaluation of K .

The formula usually adopted,

$$K = \frac{1}{t} \log \frac{a}{a-x},$$

necessitates an initial reading giving the value a at any arbitrary time t_0 and a subsequent series of readings giving a series of values of $a-x$ after times t_1, t_2, t_3 , etc. It is obvious that any error in the initial value affects all the values of K and also that as t increases observational errors are gradually obscured. On this account, a comparatively even set of values of K may be deduced from tolerably inaccurate observations. There is the additional disadvantage that any real divergence from constancy in the value of K will tend to be obscured. The difficulties are overcome by using the formula in the slightly different form:

$$K \log e = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2},$$

deducing values of K for equal intervals of time.

To obtain values of K of convenient magnitude, $K \log e$ is multiplied by 10^5 . The values of K given in subsequent tables are always those of $K \log e \times 10^5$, the unit of time being 1 minute.

In this way any error common to the series, due to an error in

the initial reading, is obviated; moreover, by making the interval of time as small as the accuracy of the observations will allow, any change in the value of K due to a departure from the unimolecular law becomes more obvious. If the interval of time be small, the sugar will be the only variable during the interval, the change in the water being negligible. It is legitimate therefore under such conditions to treat the interaction as unimolecular; any departure from the law will be shown by differences in the values of K at different periods, as changes in other factors than the sugar become significant.

The values of K found by means of the above formula, using the corrected end-points, show a marked regular rise as hydrolysis proceeds; previous observers appear to have overlooked this change.

The following example may be quoted in illustration. The experiment was one in which one molecular proportion of hydric nitrate and one of sugar were dissolved in sixty molecular proportions of water.

TABLE I.

Time from mixing in minutes	15	20	25	30	35	40	45	50	55	75	95
K	425.8	426.0	427.6	428.0	428.7	430.5	430.9	431.6	431.8	432.5	435.7

The values of K are shown by this example—only one of the many that might be quoted—to be inconstant. In less concentrated solutions the rise in the value of K is not so great but becomes imperceptible only in very dilute solutions.

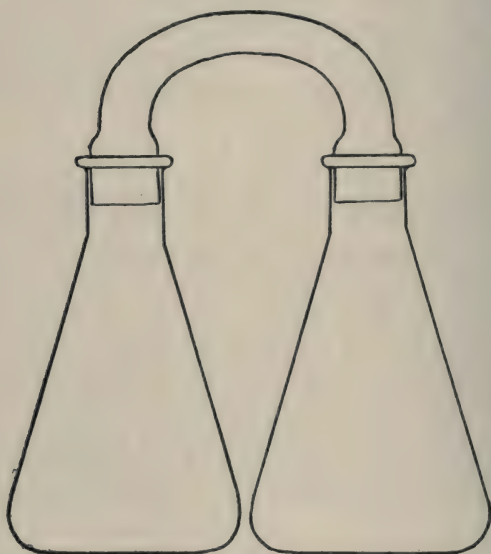
The method ordinarily adopted, by which the ultimate value of K is taken to be the mean of the various separate values, is clearly one which cannot be followed legitimately except in the case of dilute solutions: each separate value of K corresponds presumably with some particular condition of the solution in which changes are proceeding.

If the rates of hydrolysis in different experiments under different conditions are to be compared, it is essential that the value of K corresponding with some particular condition should be determined: from this point of view, the value at the very commencement of the interaction is obviously that which it is most desirable to determine. It is arrived at in the following way.

The solutions of sugar and of acid are prepared and mixed in the apparatus shown in Fig. 1. This consists of two 100 c.c. Jena flasks connected by a bent tube, of wide bore, the ends of which are carefully ground to fit into the necks of the flasks. The acid is weighed into one flask and sugar into the other together with the amount of water necessary to effect the degree of dilution desired. The solutions can be kept unmixed in such an apparatus until required

and then heated to the temperature at which the experiment is to be made and thoroughly mixed at that temperature without risk of loss by evaporation. The mixture is quickly transferred to the polarimeter tube and readings are taken as soon as the temperature is deemed to be constant. Values of K are then determined 15, 20, 25, 30, etc., minutes after mixing, the time interval $t_2 - t_1$ being made as short as the observational error will allow. From these values, the value of K at the time 0 is found by extrapolation. Very great care and practice are required to secure sufficiently regular values; it is only when every attention is paid to the

FIG. 1.



adjustment of the temperature and to all recognisable sources of error that really trustworthy results are secured.

The value of K thus determined is independent of the other changes going on in the solution. It is a measure of the rate of inversion, under definite known conditions of concentration of sugar, acid and water, at the commencement of the period of change when the products of change are without influence. This value alone will be given throughout this communication.

In the case of the example quoted above, the value at the time of mixing found by extrapolation was slightly below 424. The method generally used does not involve particular care being taken to obtain observations immediately after mixing but an interval,

perhaps thirty minutes, is allowed to lapse before the initial reading is taken; consequently, the values of K found by the ordinary method are those at times beginning more than forty minutes after mixing and continuing later than in the case of the above example; the values of K deduced by the method would lie somewhere between 430 and say 438, giving a mean very different from the initial value arrived at by the method advocated in the previous section, namely, 424. In more concentrated solutions than that referred to, the rate of alteration of the end-point would be greater and the increase in the value of K greater, thus introducing the possibility of still larger errors.

In this connexion, it is necessary again to emphasise the extreme importance of a correct determination of the end-point, as a small alteration in its value causes a large alteration in each value of K . Moreover, by slightly raising the end-point, the values of K are raised, the later to a greater extent than the earlier; lowering the end-point has the effect of reducing the value of K , the later values being those most affected. It is therefore obvious that in a case in which the values of K should actually be of constant magnitude, they may appear to rise or fall if the end-point determined be too high or too low.

Before the method of correcting the end-point by extrapolation had been devised, acting under the belief that has been accepted hitherto that a constant may be obtained by applying the unimolecular equation, attempts were made to deduce constant values of K by taking some value lower than that observed, which was obviously too high in many cases. It was found that if the observed values were but slightly adjusted, K could be made practically constant, varying in some cases less than a single unit, over a considerable range, in a constant of 800. When, however, the corrected end-point was deduced in the manner explained above, it was evident that the adjustment required to make K constant was not in correspondence with the observed rate of rise due to the secondary change but considerably greater. Moreover, when the change was followed over a greater part of its course than is customary, by adjusting the end-points constant values of K could be deduced only during the middle period—the period during which it has been customary to make the observations—thus emphasising the danger of making deductions from the study of an interaction over a narrow range.

It is more than probable that in the past “constant” values have not infrequently been arrived at because the impression has prevailed that the values should be constant and departures from uniformity have been interpreted as experimental errors.

It remains to point out that the method advocated is applicable only to the earlier periods of change during which the magnitude of the effect produced by the secondary changes is negligible. It is unfortunate that this is the case, as several of the issues to be decided cannot be discussed satisfactorily without the knowledge of the course taken by the change throughout the entire period.

Nature of the Interaction.

The rise in the values of K in the example given in table I cannot be attributed to the alterations made in the observed end-point, as the corrections introduced have involved the lowering of the observed end-point: consequently the later values of K are reduced to a greater extent than the earlier values—in other words, if no alterations had been made in the end-points, the rise in the values of K would have been still greater.

A question now to be considered is whether the increase in value of K cannot be explained by the change in the active mass of the water. It has always been assumed that the hydrolysis of cane sugar is a bimolecular change in which sugar and water both take part and that when the change in the concentration of the water becomes significant the rate of hydrolysis is expressed by the equation:

$$\frac{dx}{dt} = K'(a-x)(b-x),$$

($b-x$) representing the active mass of water.

In any experiment, the several values of K deduced from the unimolecular equation:

$$\frac{dx}{dt} = K(a-x) \text{ are those of the ratio } \frac{\frac{dx}{dt}}{a-x}.$$

In the bimolecular equation, this ratio is equal to $K'(b-x)$; K' being by hypothesis constant throughout the experiment, $K'(b-x)$ must decrease as the water is used up during hydrolysis. In point of fact, instead of diminishing, it increases: plainly showing that taking into account the change of active mass of the water would merely accentuate the want of constancy: in other words, the hydrolysis of cane sugar by acids cannot be treated as a simple case of bimolecular change in which merely water and sugar are the interacting substances.

Besides the reduction in the active mass of the water, other important changes take place as hydrolysis proceeds. In place of each molecule of cane sugar, two hexose molecules come into existence; changes also take place in the degree of association of the

various substances present in the solution; the ratio of acid to water also increases as water is used up; lastly, it is well known that although the rotatory power of cane sugar and of dextrose is but slightly affected by changes of concentration, that of *lævulose* is subject to considerable change. The changes in optical activity to be considered, however, are not merely those which the various substances undergo in simple solutions; the task is the far more difficult one of taking into account the changes which take place under the reciprocal influence of the various substances in solution—of the acids as well as of the various sugars.

The alteration in the value of K as the interaction proceeds is undoubtedly the algebraic sum of all such influences as have been referred to. It is improbable that the separate effect of each of the influences pictured can be evaluated. It cannot be too clearly emphasised, therefore, that no positive deduction can be made from the fact that K either remains constant or alters in value during the course of an experiment—on account of the numerous secondary influences, which increase in magnitude as the change proceeds.

Moreover, if the influences referred to either detract from or increase the optical rotatory power of the solutions, it cannot be asserted that the optical change affords a true measure of the course of chemical change: if the rate of change in optical characters be not strictly proportional to the rate at which the chemical change proceeds, it is obvious that the results arrived at are not those sought for and do not afford a strict measure of the rate of chemical change.

Whilst therefore the initial values of K determined by the optical method under different conditions may be used in comparing the changes which set in under these different conditions, it would seem that the method is of less value in studying the changes which the sugar itself undergoes under any particular set of conditions in an individual experiment.

Although by far the most accurate as well as the simplest method of following the course of change, apparently the polarimetric method is an unsuitable method, if the object be to arrive at a quantitative interpretation of the entire course of change; the chemical method, which permits of the measurement of the products of an interaction throughout the period of change, would seem to be the only one that can be used for such a purpose. Unfortunately the experimental errors incidental to chemical methods are usually so considerable that the minor departures to be detected are likely to escape observation, apart from the fact that the labour involved is usually very great.

Rate at which Cane Sugar is Hydrolysed under Different Conditions of Concentration.

Although the effect of varying the proportions of sugar and of acid has been studied more or less fully by previous workers, no systematic observations have been made on the extent to which variations over a wide range in the amount of water present affect the rate of change.

At the outset of the inquiry, therefore, three sets of experiments were carried out in each of which water was the variable, a different proportion of sugar being used in each series in order that any influence exercised by the concentration of the sugar might be discovered. In each series, a single molecular proportion of hydrogen chloride was present together with either one-quarter,

TABLE II.

Hydrolysis of Cane Sugar by One Molecular Proportion of Chlorhydric Acid.

	Sugar.					
Water.	$\frac{1}{4}$ molecular proportion. K.		$\frac{1}{2}$ molecular proportion. K.		1 molecular proportion. K.	
30	1282	1282	1276 1278	}	1277	
40	808 806 806 804	806	815.5 818.5		}	817
50	583 578 579	580	585 580	}	582.5	579 582
60	449 448	448.5	455.5 455.5	}	455.5	450 455
80	303.5	303.5	307		307	307.5
100	228 229	228.5	230 229		229.5	228 230
200	100.5	100.5	101		101	101

one-half or a single molecular proportion of sugar in a solution containing from 30 to 200 molecular proportions of water. As in all other cases considered, the action took place at 25°. The results are recorded in table II.

Influence of the Concentration of the Sugar.

The values of *K* given in the table are deduced from experiments made before the method of calculation explained in a previous section was developed. As the readings were taken some time after

mixing the solutions, it was impossible to deduce initial values by extrapolation. In order to obtain comparable data, values of K were determined at the stage of change when the action was approximately one-half or three-quarters complete; it was therefore possible to infer what amount of water was present and to deduce the value corresponding with a definite concentration. When subsequently the form of the curve expressing the relationship between the values of K and the concentration of the acid was ascertained, values were calculated by interpolation for solutions of the strength prepared; these are given in the table.*

The experimental errors involved in the determination are probably greater in the case of solutions containing one-half and a single molecular proportion of sugar, as these were first examined before practice had been gained in utilising the various refinements referred to in the previous communication.

It is evident that changes in the concentration of the sugar have very little effect on the value of K at any of the dilutions considered. It is impossible to say from the numbers whether the effect be to increase or to decrease the value as the concentration of the sugar is increased from one-quarter to one molecule or whether there be no effect at all. The values obtained in the case of the solutions containing half a molecular proportion of sugar are apparently the highest but, as already pointed out, the errors may well have been greater in this series than in the others; in fact, this must be assumed to be the case, judging from later experience.

It is clear that when the solutions are dilute, the effect of considerable variations in the concentration of the sugar is extremely small. Later on, when the method had been fully developed and more skill had been gained in carrying on the observation, the effect of an alteration of the concentration of sugar was again considered—this time over a much wider range of concentration of sugar. In the solutions examined, the water and acid (nitric) were kept at a molecular concentration of 60 and 1 respectively, whilst that of the sugar was varied from 0.1 to 2.5. The results obtained are displayed in table III and also in Fig. 2. They upset the accepted belief that the rate of hydrolysis is proportional to the concentration of the sugar when sugar is the only variable.

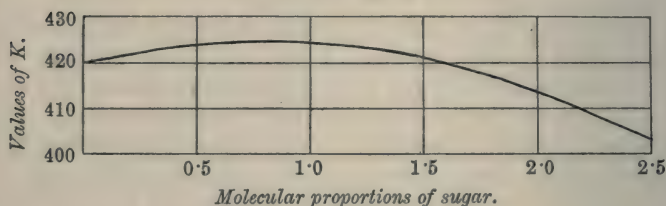
* These values are to be regarded as approximate, as the method by which they are deduced involves the assumption that the rise in the values of K is conditioned only by the disappearance of water and the consequent concentration of the acid, any other possible cause of alteration in the values of K being left out of account. In the case of experiments with the smallest proportion of sugar ($\frac{1}{4}$ molecular proportion), the errors involved must be very small, as in the more dilute solutions of this series no appreciable rise is manifest in the values of K throughout an experiment; even in those containing a small proportion of water the increase is not great.

TABLE III.

Sugar.	K .	Mean.
0.1	421	421
0.25	422	422
1.0	424	424
1.5	421	
2.0	412	413
	413	
2.5	403	403

As the concentration of sugar is increased, the value of K at first rises slowly, reaching a maximum when the molecular concentration of sugar is approximately unity; it then decreases somewhat

FIG. 2.



rapidly as the concentration of sugar is further increased. This behaviour is probably conditioned by a variety of causes and cannot well be regarded otherwise than as proof that the change usually considered so simple is in reality of a very complex character.

The change in concentration of the sugar as the sugar disappears in any experiment must affect the successive values of K but the method by which K is arrived at, explained in a previous section, serves to eliminate this effect, as the value determined is that which characterises the solution at the commencement of change.

Degree of Hydration of the Acid System.

It is generally recognised that the rate at which sugar is hydrolysed by acids is roughly proportional to the concentration of the acid. Nevertheless, it is very difficult to discuss the exact way in which the activity of an acid varies with the concentration, as it is clearly impossible to vary the concentration of an acid in a known way. In an aqueous solution, the acid is combined with and in some way controls more or less of the water, so that if different amounts of acid be present the amount of uncombined water will vary according to the amount of acid present: the amount of water combined in the acid system being unknown, it is practically

impossible to arrange that a definite proportion of free water shall be present in a given solution of the acid.

The data used in discussing this question are derived from experiments with chlorhydric and nitric acids, in which only a

FIG. 3.

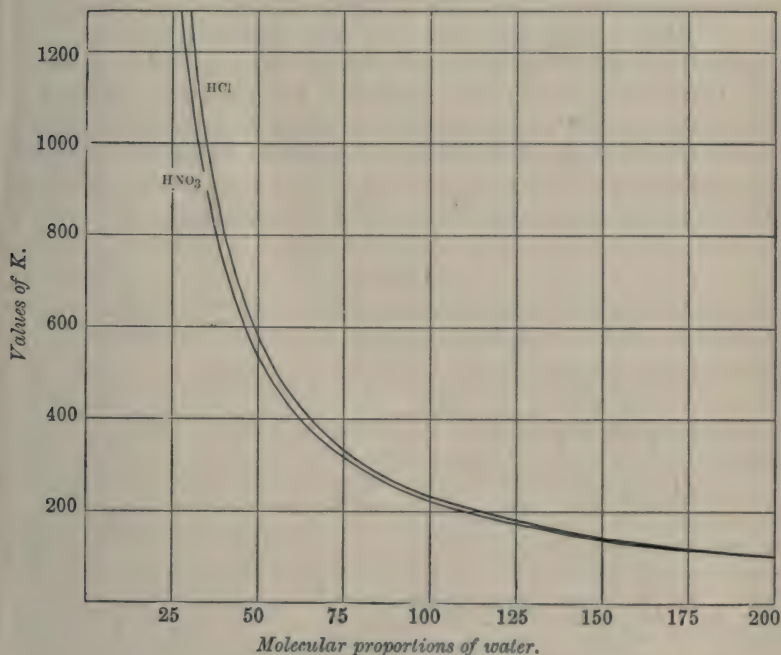


TABLE IV.

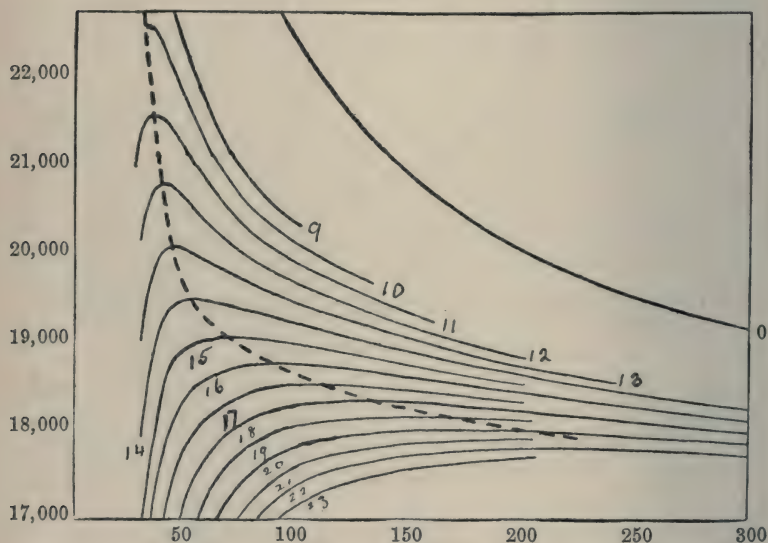
Hydrolysis of Cane Sugar (1/4 Molecular Proportion) by One Molecular Proportion of Nitric Acid.

Water.	K' .	Mean.
30	1126	1126
40	741	740
	739	
50	540	540
	543	
	538	
60	422	422
	422	
80	292.2	292.4
	292.6	
100	223.1	222.9
	222.7	
200	100.1	100.1
300	63.8	63.8

quarter-molecular proportion of sugar was used; the values are those given in tables II and IV. They are shown graphically in Fig. 3.

The rough proportionality between the values of K and the concentration of the acid which is obvious on considering the results recorded in tables II and IV is of such a character as to favour the assumption that the divergence from true proportionality may possibly be due to the disappearance of water and that if allowance were made for the combined water proportionality would become obvious. This consideration has led to a novel method of discussing the results being devised; the results obtained by the application of this method are not only highly interesting but appear to be of a rational character.

FIG. 4.



The method is best explained by reference to Fig. 4. Along the horizontal axis is given the total water present in molecular proportions (one molecular proportion of acid being always present), whilst along the vertical axis is given a set of values of the product of K into the number of molecules of water left free on the different assumptions that are possible as to the number of molecules controlled by the acid. The diagram is best understood by considering an individual curve—say that numbered 14. This curve, which is the outcome of the assumption that 14 molecules of water are associated with one of acid, was arrived at in the

following way. The successive values of K deduced from observations with solutions containing 30, 40, 50, 60, etc., molecular proportions of water were multiplied by 30-14, 40-14, 50-14, 60-14, etc., respectively; each product was then indicated on the ordinates through 30, 40, 50, 60, etc. The other curves were arrived at by assuming that the number of molecules expressed by the number on the curve was controlled by the acid.

What was sought for was the condition of hydration when K was proportional to the molecular concentration of the "acid system"—in other words, the *hydrated* acid.*

As the "degree of hydration" probably increases as the solution is diluted, there can be only one concentration corresponding with a particular point on each curve at which the degree of hydration is that assumed. In the more concentrated regions on the left, the rise in the curve is an indication that the product of K into free water increases as the solution is diluted; whilst in the weaker solutions the fall of the curve is an indication of the decrease of this product. At the maximum, the product neither increases nor decreases; this may be regarded as the point sought for.

As a greater degree of hydration is assumed, the positions of the maxima on successive curves occur at points indicative of greater degrees of dilution—in other words, the acid system is more highly hydrated the greater the degree of dilution. The result is one which is to be anticipated on general grounds. A curve drawn through the several maxima expresses the change in the value of the product of K and free water (in other words, the ratio of K to the concentration of the hydrated acid) as the degree of hydration increases as the solution is diluted; moreover, it expresses the fact that not only does the system vary in composition and become more hydrated but also that it diminishes in activity as dilution proceeds.

Table V gives the values which we shall call the apparent hydration values of the acids for chlorhydric acid and for nitric acid as the total water is increased and also the corresponding molecular hydrolytic activities of the acids.

It should be pointed out that the water controlled by the sugar

* The expression molecular concentration of the acid is here used to imply the molecular ratio of acid to *free* water. Thus in a solution prepared with 40 molecular proportions of water and one of the acid hydrolyst, assuming this to be associated with n molecules of water, the concentration is $\frac{1}{40-n}$. The ratio of K to

this concentration is obviously $K(40-n)$. These are the values made use of in plotting the curves in Fig. 4. The "acid-system" must be supposed to include the hydrolyte with its attached water; in fact the whole of the water that is not free, either because it is attached or controlled; the assumption is made moreover—which is probably not a correct one—that the free water is ordinary water.

TABLE V.

Apparent Molecular Hydration Values of Chlorhydric and Nitric Acids at different degrees of dilution and the corresponding molecular hydrolytic activities of the acid systems.

Dilution (molecular proportions of water to one of acid).	Apparent molecular hydration.		Relative molecular hydrolytic activities.	
	HCl	HNO ₃	HCl	HNO ₃
30	12.4	10	225	225
40	13.6	12.3	211	205
50	15.1	13.8	202	196
60	16.8	14.6	193	192
80	18.7	15.7	186	188
100	19.8	16.6	182	186
200	—	20.0	—	180

is not taken separately into account, the values arrived at being those for the total water controlled. As, however, the concentration of the sugar was very small in the experiments from which the values of K were derived and as sugar is probably not largely hydrated, the portion of the water not associated with the acid is probably very small. In order to eliminate this it would be necessary to work from values of K corresponding with infinitesimal concentrations of sugar.

The results of similar experiments carried out by E. Wheeler using cane sugar and hydrogen bromide and iodide and by W. H. Glover using raffinose and hydrogen chloride, hydrogen bromide and hydric nitrate have been discussed in a similar way and similar results have been arrived at—the degree of hydration of the acids always following the order of their activities. Moreover, the hydration values arrived at from W. H. Glover's experiments in which raffinose was used as the hydrolyte are practically the same as those arrived at by using cane sugar in the case of both the acids used—this is an important confirmation of the validity of the method. These results will be discussed in parts XIV and XVII.

Lastly, attention may be drawn to the remarkable similarity in the values given in table V as the relative molecular hydrolytic activities of the two acid systems in solutions containing equal total amounts of water. To determine the precise relationship of the two acids, it will be necessary to amplify the data so that the values are placed beyond question.

Effect of Salts on the Rate of Hydrolysis by Acids.

Apparent "hydration" values have been deduced for salts by Caldwell, Whympier and others, who found by trial how much

water must be added to a system containing water, sugar, acid and salt to reduce the hydrolytic activity of the system to that of a similar system from which salt was absent. A set of values for different salts was arrived at in this way but only one dilution was studied. The method has been applied to a larger number of salts in solutions varying considerably in concentration.

The rate of hydrolysis was determined, as in the case of the acid alone, in solutions containing one molecular proportion of acid, one-quarter of sugar, one of salt and 60, 80, 100 respectively of water. In the case of chlorhydric acid, the chlorides of lithium, sodium, rubidium and caesium were examined; in the case of hydric nitrate, the nitrates of lithium, sodium, potassium, rubidium, caesium, silver and calcium. The results are recorded in tables VI and VII. As the value of K is always increased by the presence

TABLE VI.

Influence of Chlorides on the Rate of Hydrolysis of Cane Sugar by Chlorhydric Acid. Sugar $\frac{1}{4}$, acid 1, salt 1, water 60, 80 and 100 molecular proportions.

Water.	K				
	HCl alone	LiCl	NaCl	RbCl	CsCl
50	580	—	833	—	—
60	448·5	628	610	576	562
80	303·5	395	388	370	364
100	228·5	284	280	270	267

TABLE VII.

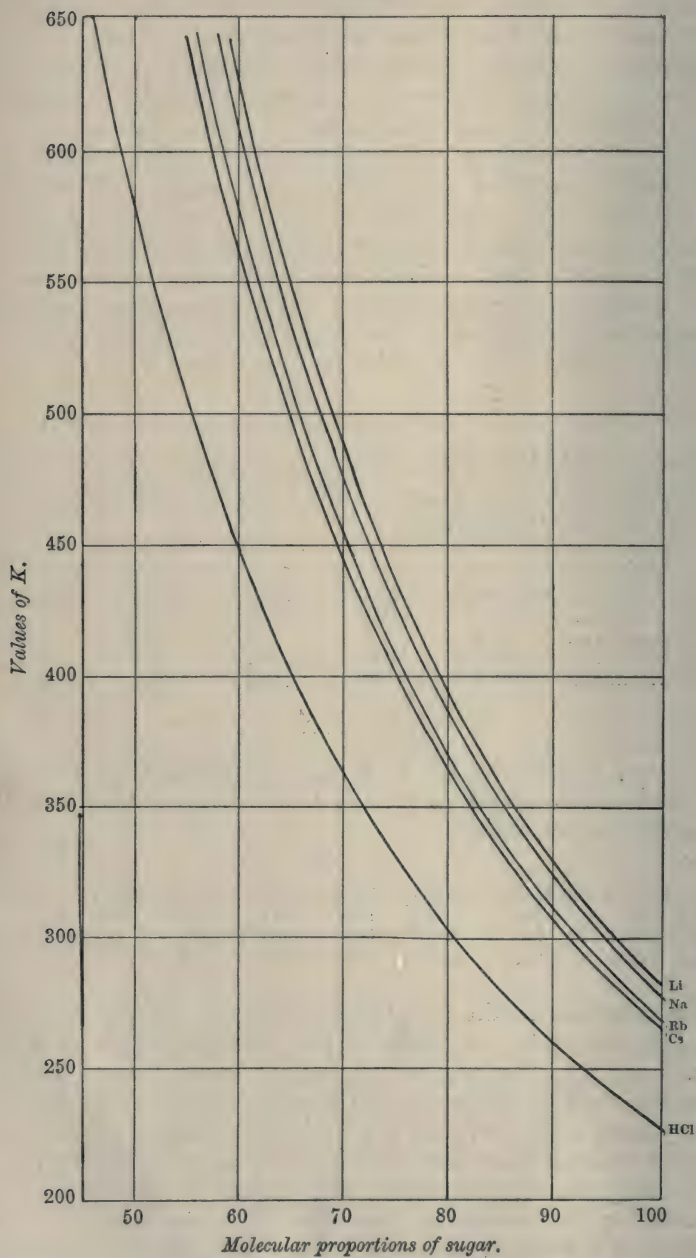
Influence of Nitrates on the Rate of Hydrolysis of Cane Sugar by Nitric Acid. Sugar $\frac{1}{4}$, acid 1, salt 1, water 60, 80 and 100 molecular proportions.

Water.	K						
	HNO ₃ alone	LiNO ₃	NaNO ₃	KNO ₃	RbNO ₃	CsNO ₃	Ca(NO ₃) ₂
60...	422	565	534	504	495	486	476
80...	292·4	368	353	339	335	331	321
100...	222·9	269	261	252	251	247	—
							303

of salts, when the results are plotted graphically the curves for the salts lies always to the right of the corresponding acid curve (Figs. 5 and 6). The apparent hydration values for any salt for any dilution within the range of the experiments can be read off directly from such curves as the horizontal distance between the curve for the particular salt and that for the corresponding acid.

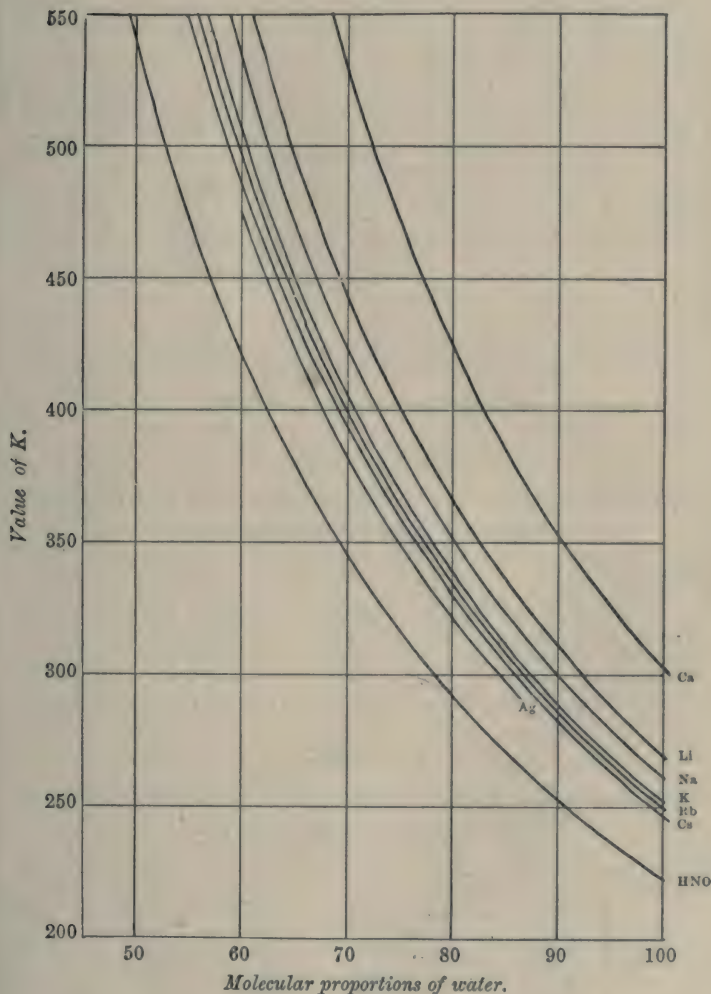
Previously the apparent degree of hydration of the salt has been expressed as the molecular proportion of water that must be added when the salt is present to reduce the value of K to that found in the absence of the salt. It is obviously a better method

FIG. 5.



of comparing the apparent hydration values of salts at different dilutions to deduce the degree of hydration of the salt in a solution that has the degree of activity which the acid exercises in the solution to which the salt is added when testing its efficiency—in

FIG. 6.



other words, to give as the apparent hydration value the number of molecular proportions of water n which appear to be controlled by a single molecular proportion of the salt in a solution composed of x molecular proportions of water together with a single molecular

proportion of the salt. The apparent hydration values so determined of the chlorides and nitrates are shown in tables VIII and IX, the values of the acids being also given to facilitate comparison. Fig. 7 shows the results graphically in the case of nitric acid and nitrates.

Fig. 7.

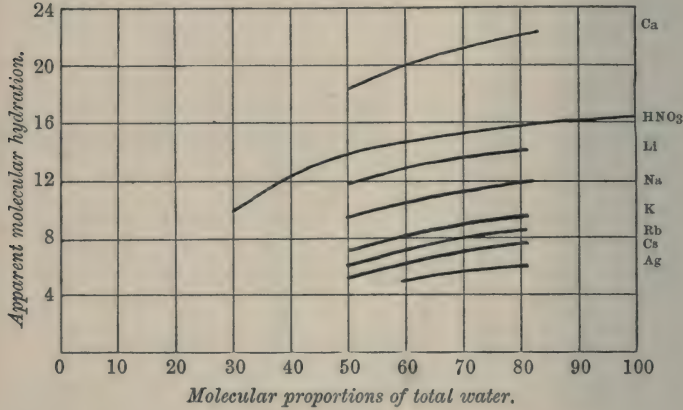


TABLE VIII.

Apparent Hydration Values of Chlorhydric Acid and Chlorides at Different Degrees of Dilution.

Dilution.....	60	80	100
(molecular proportions of water)			
Apparent hydration values { HCl	16·8	18·7	19·8
{ LiCl	13·3	14·9	16·5
{ NaCl	12·3	14·0	15·6
{ RbCl	10·3	11·6	13·1
{ CsCl.....	9·4	10·7	12·3

TABLE IX.

Apparent Hydration Values of Hydric Nitrate and Nitrates at Different Degrees of Dilution.

Dilution	60	80	100	200
(molecular proportions of water)				
Apparent hydration values { HNO ₃	14·6	15·7	16·6	20
{ LiNO ₃	11·3	13·3	14·3	
{ NaNO ₃	9·6	11·2	12·4	
{ KNO ₃	7·6	9·0	10·0	
{ RbNO ₃	6·9	8·3	9·4	
{ CsNO ₃	6·1	7·6	8·0	
{ AgNO ₃ ..	5·3	5·8	—	
{ Ca(NO ₃) ₂	—	20·4	22·3	

In the case of chlorides and nitrates of the alkali metals, the apparent hydration values decrease as the atomic weight of the

metal in the salt increases. This may be due to the fact that the effect of the salt on the rate of hydrolysis is due to a variety of causes acting in opposite directions, among others to a concentrating effect—conditioned by a withdrawal of water by the salt—which increases the rate of hydrolysis and to a mechanical effect tending to diminish it: this mechanical effect probably increases as the mass of the molecule increases; moreover salts are probably present in solution to a greater or less extent in the form of “associated” molecules. For these various reasons it is impossible at present to institute any effective comparison between salts in explanation of the observed differences in the degree of hydration.

Attention may be drawn to the similarity between the curves for the hydration values of the salts and those of the corresponding acids; this may be regarded as confirmation of the validity of the method of arriving at the degree of hydration of acids advocated in this communication.

Summary.—Owing to the improved appliances available, the hydrolysis of cane sugar by acids has been studied more thoroughly and with closer approach to accuracy than has before been possible. It has been found not only that there are unexpected sources of error in the method adopted by previous workers but also that the accepted views which have hitherto guided inquirers in this field need modification in essential particulars.

The chief points in the present communication are the following:

(1) The end-point usually observed when the sugar is judged to be entirely inverted is not the true end-point but an erroneous value, as the rotatory power at the end of the hydrolysis does not remain constant but gradually becomes less and less negative, on account of a secondary change affecting the products of hydrolysis. Although probably it is unimportant in the case of dilute solutions, this change cannot be neglected in concentrated solutions; in the case of such solutions, the corrected end-point must be deduced from observations of the rate of change after the rise sets in.

(2) The values of K obtained by applying the unimolecular equation $dx/dt = K(a - x)$, except in the case of very dilute solutions, are not constant but rise as hydrolysis proceeds; in other words, the action does not follow the unimolecular law. Moreover, if the action be treated as a case of bimolecular change in which the rate of change is proportional to the mass of water present as well as to the amount of sugar, no better result is arrived at, the rise in the values of K thus deduced being greater than when the unimolecular expression is applied.

(3) The usual method of applying the mass-action equation is

not the best. Besides a possible general error due to an incorrect initial reading, it gives a spurious constancy to the values of K , making it difficult to detect actual departures from the unimolecular law. A better way of applying the equation is in the form:

$$K \log e = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2},$$

where $a - x_1$ and $a - x_2$ are the sugar concentrations at times t_1 and t_2 respectively—successive equal intervals of time being taken as small as the accuracy of the observations allows or the rapidity of the change demands.

(4) The observations are most satisfactorily dealt with by deducing values of K by the unimolecular equation for successive small intervals during each of which sugar is the only significant variable. If the successive values of K rise as hydrolysis proceeds, the value at the commencement of the change when the solution is of known composition and free from products of change should be found by extrapolation. Values of K must be obtained as near the beginning of the interaction as possible; for this purpose, it is essential that the solution should be mixed at the temperature at which the experiment is to be made and readings of the rotation taken as soon as constant temperature can be obtained.

(5) It has been found that the fundamental assumption that the rate of hydrolysis is proportional to the concentration of the sugar is only an approximation. If sugar be made the only variable in a series of experiments, the values of K at first rise slowly and after reaching a maximum fall rapidly as the concentration of the sugar is increased. In studying the effect of acids and salts or other substances on the rate of hydrolysis, it is essential to use as low a concentration of sugar as possible, as the effect of the change in the sugar is practically negligible in weak solutions.

(6) From the rate of change of K when the concentration of the acid is varied, a method has been developed by means of which the apparent degree of hydration of the acid at different dilutions may be determined. This increases with dilution towards a maximum and at the same time the molecular hydrolytic activity of the acid decreases towards a minimum.

(7) From the influence of a number of chlorides and nitrates in increasing the rate of hydrolysis brought about by chlorhydric and nitric acids respectively, apparent hydration values of the salts have been determined at different dilutions. The values so determined are probably low on account of mechanical inhibiting effects and other influences exercised by the salts—they are less in the case of chlorides and nitrates of the alkali metals than in those of

the corresponding acids and decrease as the atomic weight of the metal increases.

(8) This investigation emphasises the need of taking into account the complexity of the changes involved in the hydrolysis of cane sugar under the influence of acids and shows the futility of attempting to express the rate of such an interaction by any simple mathematical equation. Although the rate of hydrolysis is nearly proportional to the concentration of the sugar and to the concentration of the *hydrated acid*, a true mathematical expression of the rate under various conditions of concentration of the interacting substances would involve, besides factors for the concentration of the sugar and the hydrated acid, numerous other factors allowing for the fact that the rate of hydrolysis is not strictly proportional to the concentration of the sugar and that the degree of hydration of the acid and also its molecular hydrolytic activity alter on dilution; in addition it would be necessary to take into account the effect of the primary products of change as well as their further change and also changes in the state of aggregation and changes in the optical rotatory power of the various components of the solution; it is obviously undesirable to attempt such an expression. Many of these factors influencing the rate of change are no doubt extremely small but may not be negligible under all conditions.

It is hoped that this investigation will have thrown light on the chief laws regulating the rate of hydrolytic change and that it may serve to indicate clearly what are the conditions under which it is legitimate to use the hydrolytic process as a means of studying the problems afforded by solutions.

XLVI.—*Studies of the Processes Operative in Solutions* *Part XIV. The Determination of Apparent* *Hydration Values by means of Raffinose.*

By WALTER HAMIS GLOVER, Ph.D., Salters' Company's Research Fellow, City and Guilds of London Institute, Central Technical College.

THE present communication contains the results of a number of observations on the hydrolysis of raffinose, a triose having the formula $C_{18}H_{32}O_{16} \cdot 5H_2O$, by nitric acid, chlorhydric acid and bromhydric acid and of the influence of certain salts of these

acids, in particular the salts of the alkali metals, on the velocity with which the sugar is converted into melibiose and fructose. The investigation was carried out primarily with the object of ascertaining whether and to what extent the substitution for cane sugar of raffinose—a compound which is similar to it in chemical properties—is attended by a difference in the apparent “hydration values” of the salts. Brief reference has been made by Armstrong and Crothers (Part VIII, p. 110) to the result of an experiment which appeared to indicate that the concentrating effect produced by the addition of one molecular proportion of sodium nitrate to an aqueous solution of one molecular proportion of nitric acid and one-quarter molecular proportion of raffinose is not so great as that induced when the hydrolyte is cane sugar; in other words, the “hydration value” of sodium nitrate determined by hydrolysing raffinose by nitric acid in the presence of sodium nitrate was $8\text{H}_2\text{O}$ instead of $11\text{H}_2\text{O}$, the value obtained by Whympers by means of cane sugar (Part III, p. 579). A difference of this nature was not altogether surprising when viewed in the light of the results recorded by Armstrong and Watson (Part IV). It is shown in this paper that the “hydration values” determined with the aid of methyl acetate are vastly different to those deduced from the hydrolysis of sucrose. It may be stated at once, however, that the “hydration values” derived from the experiments with raffinose are almost identical with those arrived at when cane sugar is used as the hydrolyte in the case of chlorides, although in the case of the nitrates the values are uniformly slightly smaller.

Before proceeding further with the discussion on the effect of salts on the rate of hydrolysis of raffinose by acids, it will be advisable to contrast the behaviour of cane sugar and raffinose towards acids from the point of view of the readiness with which the fructose section of the sugar molecule is split off.

The course of the interaction between one molecular proportion of acid and a one-quarter molecular proportion of raffinose in aqueous solution has been investigated, the proportion of water ranging from 40 to 100 molecules; the results are recorded in table I. It will be seen that the velocity, as represented by $K(1/t \log a/a-x)$, is not inversely proportional to the quantity of water present; instead, the product $K \times$ number of molecules of water becomes smaller as the dilution of the interacting substances becomes greater. Neither does the “volume molecular hydrolytic activity”* of the acid remain constant. In order to arrive at this

* “Volume molecular hydrolytic activity” = $K \times$ vol. in litres containing 1 gram-molecular proportion of acid; it represents the rate at which the sugar would be hydrolysed provided 1 litre of the solution contained 1 molecular proportion of acid having the same activity as that in the solution under investigation.

quantity, the densities of the solutions at 25° containing 1 molecular proportion of nitric acid and 0.25 of a molecular proportion of raffinose (anhydrous) in 50 and in 100 molecular proportions of water were determined and found to be 1.0802 and 1.0425 respectively; from these values the volumes of the solutions were calculated to be 1008.2 c.c. and 1907.9 c.c. respectively; assuming the hydrolytic activity of the acid to be proportional to the concentration of the acid per unit volume, we have

$$K_1 = 458.7(485 \times 1.0082)$$

and $K_1 = 354.8(186 \times 1.9079)$ as the "volume molecular hydrolytic activities" of the nitric acid at the two dilutions. The fact that the addition of 50 molecular proportions of water (900 grams) to the stronger solution increases the total volume by approximately its own volume is not without interest.

The apparent hydration values have been deduced by means of the method developed by F. P. Worley, in Part XII of these studies. On contrasting the values with those obtained by Worley using cane sugar as hydrolyte, it is obvious that the two sugars afford practically identical values.

It is extremely difficult to interpret such results, as although a fairly simple relationship exists between the rate of change of the sugar and the amount of "free" water (total water - x), there can be little doubt that dilution is accompanied by a great many changes in the complexity and nature of the components of the system under examination. The nature of many of these changes has been discussed in Part VI of these studies; the following may also be cited as exemplifying the great variety of changes which possibly accompany any alteration in the molecular proportions of the components. The hydrolysis of a sugar by an acid undoubtedly takes place in an unstable system containing acid, sugar and water; one effect of an increase in the proportion of water would be to dissociate or retard the formation of this system and consequently to diminish the "molecular hydrolytic activity" of the acid.

Before leaving the subject of the hydrolysis of raffinose by acids, attention must be drawn to a remarkable relationship which exists between the rates at which cane sugar and raffinose are hydrolysed. In the case of the three acids used in this investigation, it is found that cane sugar is always hydrolysed by the same solution of an acid at a rate 1.195 times (mean value) greater than raffinose; this is shown by the following table:

Molecules of water.	Values of $\frac{K \text{ (cane sugar)}}{K \text{ (raffinose)}}$		
	HNO ₃ .	HCl.	HBr.
40	1.193	1.199	1.195
50	1.185	1.203	1.184
60	1.196	1.198	1.186
70	1.192	1.186	1.200
80	1.196	1.193	1.201
90	1.200	1.203	1.203
100	1.194	1.194	1.194
Mean	1.194	1.196	1.195

The fact that the cane sugar section of the molecule of raffinose is less readily hydrolysed than is cane sugar itself has been explained partly by the assumption that raffinose is the weaker because it is a less hydrolated hydrolyte (compare Armstrong and Crothers, *loc. cit.*). Some experiments have been made which seem to indicate that the difference may be due largely to the degree in which combination takes place between the sugar and the acid, as indicated by the influence salts exercise on the specific optical rotatory power of sucrose and of raffinose. In each case, the proportions used were 0.5 gram-molecular proportion of anhydrous sugar + 1 gram-molecular proportion of anhydrous salt + 50 gram-molecular proportions of water, the values obtained being the following:

Sugar.	Salt.	$[\alpha]_{H_g}^{25}$		Reduction in $[\alpha]_{H_g}^{25}$ of sugar in percentages.
		Experimental values.	Mean.	
Cane Sugar.	—	78.06	78.06	—
	Potassium chloride ...	77.10	77.10	1.23
	„ bromide ...	76.48	76.48	2.02
	„ iodide.....	75.46	75.46	3.33
Raffinose.	—	145.46		
	—	145.65	145.55	—
	Potassium chloride ...	145.49		
	„ „ ...	145.51	145.50	0.03
	„ bromide ...	145.23		
	„ „ ...	145.24	145.235	0.22
	„ iodide.....	144.56		
	„ „	144.58	144.62	0.64

Assuming the change of specific optical rotatory power to be due primarily to combination of sugar and salt, as dilution has practically no effect on the specific rotatory power of either cane sugar or raffinose, it is evident that under comparable conditions raffinose does not combine to so great an extent with salts as does cane sugar; it is to be inferred therefore that acids likewise do not combine so readily with the triose as with the biose and since hydrolysis of the sugar is undoubtedly preceded by the formation of a compound of acid, sugar and water, it naturally follows that raffinose would not be hydrolysed so readily as cane sugar.

Passing now to a consideration of the results obtained in the investigation of the influence of various salts on the rate of hydrolysis of raffinose by acids (tables I, II, III), we find the concentrating effect to be almost the same as that when cane sugar is the hydrolyte. This is well illustrated by the following table, in which are given the number of molecules of water which must be added to neutralise the accelerating or concentrating effect (apparent hydration values) of the salts in the case of the two sugars.

Salt.	Total number of mols. of water present per mol. of acid and salt.	Number of mols. of water to be added to the system.	
		Cane Sugar.	Raffinose.
Silver nitrate	50.0	—	3.3
	55.5	4.7 ²	3.7
	60.0	5.0 ²	4.0
Potassium nitrate.....	50.0	7.1 ¹	6.7
	55.5	—	7.2
	60.0	8.2 ¹	7.5
Sodium nitrate.....	50.0	9.5 ¹	8.8
	55.5	—	9.3
	60.0	10.6 ¹	9.6
Lithium nitrate	40.0	—	10.0
	50.0	11.8 ¹	11.4
	60.0	13.0 ¹	12.0
Ammonium chloride..	50.0	10.2 ⁴	10.2
	55.5	10.9 ⁴	10.8
	60.0	—	11.0
Potassium chloride ...	50.0	10.8 ⁴	10.4
	55.5	11.1 ⁴	11.0
	60.0	—	11.2
Sodium chloride	40.0	10.8 ¹	10.8
	50.0	12.0 ¹	12.2
	55.5	—	13.0
Calcium chloride	40.0	22.0 ⁴	22.2
	50.0	23.2 ⁴	24.2
	55.5	—	25.0
Potassium bromide ...	40.0	10.7 ³	10.8
	50.0	12.0 ³	11.8

¹ Deduced from F. P. Worley's values.

² Whympier.

³ Wheeler.

⁴ Deduced from Caldwell's results.

The closeness of the values for the bromide and the chlorides obtained by using either cane sugar or raffinose as hydrolyte is truly remarkable; only in the case of the nitrates is a constant difference noticeable, the values derived from the use of raffinose being without exception slightly smaller than those obtained with cane sugar; it is also interesting to note that the hydration value of potassium bromide is higher than that of potassium chloride. All these observations are in accord with the explanation of the manner in which salts accelerate the rate of hydrolysis advanced in Part VIII of these studies. It is possible that part of the effect produced by

the addition of a salt to a solution of sugar and acid is due to the displacement, by the salt, of acid combined presumably with the hydroxylic and anhydride oxygen atoms of the sugar but this is not likely to be a very large effect. Neither is it probable that the retardation produced by the mechanical interference of the salt molecule is very great, although the effect produced by a series of salts, for example, the chlorides or nitrates of the univalent metals, becomes smaller as the weight or size of the molecule becomes greater.

EXPERIMENTAL.

The solutions were prepared in the flasks figured in Fig. 1, Part XII. No difficulty was experienced in obtaining the final readings: although the optical rotatory power of the solution does not remain constant at the end of the period of change under investigation, the alterations observed are too small to affect the constant K ; the optical rotatory power increases slightly at first after the chief action is completed, owing to changes of the fructose; it then decreases very slowly, possibly owing to the gradual hydrolysis of the melibiose.

Materials Used.—The sodium chloride was purified by precipitation from brine by hydrogen chloride, subsequently recrystallised from water and finally precipitated from an aqueous solution by alcohol; the ammonium chloride, potassium chloride, potassium nitrate, sodium nitrate and potassium bromide were crystallised repeatedly from water. The lithium nitrate and silver nitrate were commercially pure samples; when tested, they were found to be neutral. The requisite quantity of calcium chloride for each experiment was obtained by neutralising the calculated weight of standard hydrogen chloride solution with an excess of pure Iceland spar.

All the experiments referred to were performed at $25.01^\circ \pm 0.005^\circ$. The results obtained in two complete experiments with each acid entirely representative of the series are recorded in table IV.

TABLE I.

Hydrolysis of Raffinose by Acids.

0.25 Molecule of Raffinose (anhydrous) + 1 Molecule of Acid + a Molecules of Water.

Acid.	Molecules of water.	Values of K		Mean values of K
		Expt. I	Expt. II	
Nitric	40	620	624	622
	50	454.5	455	455
	60	357	354	355.5
	80	245	245	245
	100	185.5	185.6	185.5

TABLE I. (*continued*).

Acid.	Molecules of water.	Values of <i>K</i>		Mean values of <i>K</i>
		Expt. I	Expt. II	
Chlorhydric	40	672	672.5	672
	50	482	482.6	482
	50	375	373	374
	80	255.7	253.3	254.5
	100	192.4	190.6	191.5
Bromhydric	40	786	786.8	786
	50	555.2	556	556
	60	420	420	420
	80	277.8	278.2	278
	100	206.3	206	206

TABLE II.

Hydrolysis of Raffinose by Chlorhydric Acid in the Presence of Certain Chlorides.

0.25 Molecule of Raffinose + 1 Molecule of Hydrogen Chloride +
1 Molecule of Salt + *a* Molecules of Water.

Salt.	Mean values of <i>K</i>			
	50 molecules of water.	60 molecules of water.	70 molecules of water.	80 molecules of water.
Ammonium chloride.....	656	484	381	—
Potassium „	660	486	383	—
Sodium „	689	511	402	483.5 (62H ₂ O)
Calcium „	1035	723	539	421

TABLE III.

Hydrolysis of Raffinose by Nitric Acid in the Presence of Nitrates.

0.25 Molecule of Raffinose (anhydrous) + 1 Molecule of Nitric
Acid + 1 Molecule of Salt + *a* Molecules of Water.

Salt.	Mean values of <i>K</i>		
	50 molecules of water.	60 molecules of water.	70 molecules of water.
Silver nitrate	499	389	314
Potas-ium nitrate.....	546	421	338
Sodium „	580	442	354
Lithium „	623	473	372

*Hydrolysis of Raffinose (0.25 Molecule) by Bromhydric Acid
(1 Molecule) in the Presence of Potassium Bromide (1 Molecule).*

Molecules of water	50	60	70
Mean values of <i>K</i>	808	587	451

TABLE IV.
0.25 Gram-molecule of Raffinose (anhydrous) + 50 Gram-molecules of Water.

<i>t.</i>	+1 gram-mol. of HCl		+1 gram-mol. of HCl + 1 gram-mol. of CaCl ₂		+1 gram-mol. of HNO ₃		+1 gram-mol. of HNO ₃ + 1 gram-mol. of NaNO ₃		+1 gram-mol. of HBr		+1 gram-mol. of HBr + 1 gram-mol. of KBr	
	²⁵ a _{Hg}	<i>K</i>	²⁵ a _{Hg}	<i>K</i>	²⁵ a _{Hg}	<i>K</i>	²⁵ a _{Hg}	<i>K</i>	²⁵ a _{Hg}	<i>K</i>	²⁵ a _{Hg}	<i>K</i>
0	32.010	—	23.574	—	33.108	—	30.004	—	32.042	—	30.620	—
30	28.418	480	18.806	1039	29.330	455	26.142	581	27.956	553	25.290	808
35	27.910	483	18.292	1040	28.802	456	25.638	581	27.412	554	24.658	808
40	27.454	482	17.842	1038	28.308	456	25.174	579	26.896	555	24.082	808
45	27.012	482	17.456	1034	27.842	455	24.728	580	26.420	554	23.552	808
50	26.598	481	17.106	1032	27.394	455	24.318	579	25.968	556	23.072	808
55	26.192	483	16.782	1033	26.976	455	23.928	580	25.552	556	22.640	808
60	25.818	483	16.500	1033	26.576	455	23.568	579	25.150	555	22.238	808
65	—	—	—	—	26.196	454	23.226	580	—	—	21.870	809
70	25.130	483	—	—	25.826	455	22.916	579	24.426	556	21.540	809
75	—	—	—	—	25.478	455	—	—	—	—	21.239	809
80	24.511	483	—	—	25.162	455	—	—	—	—	—	—
90	23.953	484	—	—	—	—	—	—	23.804	555	—	—
100	23.464	484	—	—	—	—	—	—	23.244	556	—	—
110	23.026	484	—	—	—	—	—	—	—	—	—	—
120	22.636	483	—	—	—	—	—	—	—	—	—	—
∞	19.292	—	14.266	—	19.106	—	18.320	—	19.175	—	18.160	—
Means...		482.6	...	1035	...	455	...	580	...	555	...	808

XLVII.—*Studies of the Processes Operative in Solutions.**Part XV. The Changes Effected by the Reciprocal Interference of Sugars (and Glucosides) and Salts in Aqueous Solutions.*

By WALTER HAMIS GLOVER.

BRIEF reference is made by Armstrong and Crothers in Part VIII of these studies to the striking diminution of the conductivity of sodium chloride effected by the addition of raffinose. It is shown that the conductivity in a solution of a gram-molecular proportion of the electrolyte in 1000 grams of water is lowered to the extent of 21 per cent. by one-third of a gram-molecular proportion of the carbohydrate, whilst a reduction of 27.4 per cent. and 44.6 per cent. is produced by the addition of a gram-molecular proportion of glucose and cane sugar respectively. In other words, judging from these figures only, the conductivity of salts in solution is reduced by these sugars practically in proportion to the number of oxygen atoms which they contain.

The object of the investigation described in the present communication was to ascertain whether other salts are similarly affected, not only by the three carbohydrates just mentioned but also by the two reducing bioses, lactose and melibiose and by the two simple, non-reducing ethers of glucose, α -methylglucoside and β -methylglucoside. At the same time, it was considered advisable to measure the effect on the specific rotatory powers of the several carbohydrates induced by the presence of the electrolyte, particularly with the object of testing a conclusion arrived at in an earlier investigation, namely, that the specific rotatory power of a carbohydrate which is hydrolysed by acids with relative ease is influenced to a greater degree by the presence of a salt than is the specific rotatory power of a carbohydrate less open to hydrolytic attack by acids.

Preparation of Solutions.—The salts and other substances used, with the exception of the glucose and cane sugar, were purified with care. The glucose used was the purest material obtainable from Kahlbaum; the cane sugar that sold as "coffee sugar" or "centrifugals."

The solutes were weighed out in a conical Jena-glass flask, due allowance being made for the air displaced. Approximately the right quantity of "conductivity" water was then run in and the solid dissolved by gently warming the flask. After cooling to the temperature of the room, the weight of water was adjusted to the required amount on the balance. In calculating the quantity of

solvent to be added, due allowance was always made for the water already in combination with the non-electrolyte as "water of crystallisation."

Determination of Rotatory Power.—Except for certain improvements, the apparatus and methods used are described in previous communications; the measurements were made in water-jacketed tubes 400 mm. long. In cases in which the sugar undergoes mutarotation, the solutions were kept during twenty-four to forty-eight hours before the measurements were made. The specific rotatory powers recorded in this paper without exception refer to the anhydrous sugar.

Determination of Density.—The densities of the solutions at 25° were measured with the aid of the modified form of Sprengel tube described by Caldwell and Whymper (Part X).

Measurement of Conductivity.—The readings were taken with a Kohlrausch wheel-bridge, inductorium and telephone. The resistance of the electrolytic cell, the form used being that described by Caldwell and Whymper (*loc. cit.*), was as nearly as possible balanced by coils of known resistance wound non-self-inductively, so that the readings could always be taken at points close to the middle of the bridge-wire. Corrections were made for inequalities of the bridge-wire and resistance of the leads.

Effect of Salts on the Optical Rotatory Power of Glucosides and Sugars.—A vast amount of work has been done on the effect of salts on the optical rotatory power of glucose, lactose and cane sugar but much of it is valueless, as the molecular proportions of sugar and water were not kept constant; almost without exception the sugar and salt have been dissolved in water and the mixture made up to a known volume.

The specific rotatory powers of the substances used were found to be as follows:

One gram-molecule of substance in 50 gram-molecules of water.

	D_{25}^{25}	$[\alpha]_{H_g}^{25}$
Glucose.....	1.06655	+ 63.17°
α -Methylglucoside	1.05915	+ 186.50
β -Methylglucoside	1.05845	- 39.81
Cane sugar	1.11685	+ 78.08

Half gram-molecule of substance in 50 gram-molecules of water.

	D_{25}^{25}	$[\alpha]_{H_g}^{25}$
Glucose.....	1.03542	+ 62.73°
α -Methylglucoside	1.03162	+ 186.37
β -Methylglucoside	1.03127	- 39.58
Lactose	1.06634	+ 64.54
Melibiose	1.06705	+ 168.93
Cane sugar	1.06490	+ 78.06
Raffinose	1.09331	+ 145.55

The changes of optical rotatory power produced by the addition of the various salts are recorded in tables I and II.

Alteration in the Rotatory Power of Certain Sugars and Glucosides conditioned by Electrolytes.

TABLE I.

One gram-molecule of electrolyte and 0.5 gram-molecule of sugar or glucoside in 50 gram-molecules of water.

Electrolyte.	Sugar or glucoside.	Density of solutions D_{25}^{25}	Values of $[\alpha]_{H_g}^{25}$	Alteration of $[\alpha]_{H_g}^{25}$	
				In degrees.	In per cent.
Potassium chloride	Glucose	1.07958	+61.40°	-1.33	-2.12
	α -Methylglucoside ...	1.07584	+185.95	-0.42	-0.22
	β -Methylglucoside ...	1.07553	-40.30	-0.72	-1.82
	Lactose.....	1.10728	+64.65	+0.11	+0.17
	Melibiose	1.10792	+169.24	+0.31	+0.18
	Cane sugar	1.10583	+77.10	-0.96	-1.23
Sodium chloride	Raffinose	1.13128	+145.51	-0.04	-0.03
	Glucose	1.07454	+62.42	-0.31	-0.49
	α -Methylglucoside ...	1.07066	+185.85	-0.52	-0.28
	β -Methylglucoside ...	1.07084	-40.38	-0.80	-2.02
	Lactose.....	1.10247	+65.45	+0.91	+1.41
	Melibiose	1.10312	+169.38	+0.45	+0.27
Potassium bromide	Cane sugar	1.10134	+76.80	-1.26	-1.61
	Raffinose	1.12707	+145.53	-0.02	-0.02
Potassium iodide	Cane sugar	1.14179	+76.48	-1.58	-2.02
	Raffinose	1.16572	+145.24	-0.31	-0.21

TABLE II.

One gram-molecule of sugar or glucoside and 1 gram-molecule of electrolyte dissolved in 50 gram-molecules of water.

Electrolyte.	Sugar or glucoside.	Density of solutions.	Values of $[\alpha]_{H_g}^{25}$	Alteration	
				in degrees.	per cent.
Sodium chloride	Glucose	1.10231	+62.82°	-0.35	-0.56
	α -Methylglucoside ...	1.09465	+185.98	-0.52	-0.27
	β -Methylglucoside ...	1.09413	-40.55	-0.74	-1.86
	Cane sugar	1.14812	+76.94	-1.14	-1.46
Sodium nitrate	Glucose	1.11574	+62.78	-0.39	-0.62
	α -Methylglucoside ...	1.10748	+186.39	-0.11	-0.06
	Cane sugar	1.15988	+77.52	-0.56	-0.72

The following are the most noteworthy conclusions to be drawn from an examination of the figures contained in these tables: (1) The effect produced by the addition of a salt to a non-reducing sugar or a simple glucoside is to render it less dextrorotatory; that is, in the case of the dextrorotatory compounds the apparent specific rotatory power is diminished, whilst in the case of the lævorotatory

β -methylglucoside the apparent specific rotatory power is increased. Assuming the change to be produced by combination of the non-electrolyte with the salt (as the specific rotatory powers of the substances at present under discussion do not alter appreciably on dilution, the changes cannot be ascribed to a withdrawal of water from the system by the salt) and that the combination involves the formation of compounds of the type $\begin{array}{c} \text{C}-\text{C} \\ | \quad | \\ \text{C}-\text{C} \end{array} > \text{O}:\text{XR}$, the alteration

in the optical activity produced by the ethenoid link is in these cases laevorotatory. Further, in the case of closely related substances which exist in solution in only one form, it is noticeable that the compound which is most stable towards hydrolytic agents is least affected by the salt. Thus, the change of optical rotatory power of β -methylglucoside under comparable conditions is much greater than that of the α -isomeride; the β -compound is hydrolysed by acids 1.8 times as rapidly as the α -isomeride. Similarly, cane sugar, which is hydrolysed about 1.2 times as rapidly by acids as raffinose, is more affected than the latter carbohydrate, which is a derivative of cane sugar.

(2) The changes of optical rotatory power exhibited by the reducing sugars are extremely complex. The dextrorotatory bioses, lactose and melibiose, unlike all the other substances studied, become apparently more dextrorotatory in the presence of salts. Further, although in the case of the non-reducing sugars the effect produced by a molecular proportion of sodium chloride is always slightly greater than that induced by potassium chloride or sodium nitrate, the effect in the case of the reducing sugars varies considerably according to the nature of the components; thus, glucose is apparently less dextrorotatory in the presence of sodium nitrate or potassium chloride than of sodium chloride; again, potassium chloride appears to change the closely related sugars, lactose and melibiose, to practically the same extent, whilst sodium chloride has a far greater effect on lactose than on melibiose.

It is evident, then, that the effect on the optical rotatory power of a sugar or glucoside produced by the presence of a salt cannot be ascribed to any one simple cause, although the principal factor at work is undoubtedly union of the several components of the solution; the marked divergences in the case of the reducing sugars which exist in solution in two stereoisomeric forms are principally due to a change in the state of equilibrium of the isodynamic forms.

Effect of Glucosides and Sugars on the Electrical Conductivity of Salts.—The molecular conductivities of the salts used, in solutions containing a gram-molecular proportion of salt in 50 gram-molecular proportions of water, were found to be as follows: potassium

chloride, 111.44; sodium chloride, 84.35; sodium nitrate, 75.03. The molecular conductivities in the presence of the various glucosides and sugars are given in tables III and IV.

The Effect of certain Sugars and Glucosides on the Molecular Conductivities of Electrolytes.

TABLE III.

One gram-molecule of electrolyte and 0.5 gram-molecule of sugar or glucoside in 50 gram-molecules of water.

Electrolyte.	Sugar.	Molecular conductivity of electrolyte.	Reduction of molecular conductivity, per cent.
Potassium chloride	Glucose.....	92.86	16.7
	α -Methylglucoside	90.53	18.8
	β -Methylglucoside	90.77	18.5
	Lactose	78.38	29.6
	Melibiose	77.31	30.6
	Cane sugar	80.34	27.9
	Raffinose	67.38	39.5
Sodium chloride	Glucose	70.88	16.0
	α -Methylglucoside	68.94	18.3
	β -Methylglucoside	69.21	17.9
	Lactose	59.88	29.0
	Melibiose	59.30	29.7
	Cane sugar	60.82	27.9
	Raffinose	51.33	39.1

TABLE IV.

One gram-molecule of sugar or glucoside and 1 gram-molecule of electrolyte in 50 gram-molecules of water.

Electrolyte.	Sugar or Glucoside.	Molecular conductivity of electrolyte.	Reduction of molecular conductivity, per cent.
Sodium chloride	Glucose.....	59.44	29.5
	α -Methylglucoside	56.50	33.0
	β -Methylglucoside	56.80	32.6
	Cane sugar	44.16	47.6
Sodium nitrate	Glucose.....	53.28	29.0
	α -Methylglucoside	50.94	32.1
	Cane sugar	39.68	47.1

The probable manner in which sugars influence the conductivity of salts has been discussed in previous communications; the results of the experiments to be recorded in Part XVIII of these studies show, however, that although the diminution of conductivity is undoubtedly intimately connected with the number of hydroxyl groups in the molecule of the added non-electrolyte, nevertheless other factors play an important part in bringing about the diminution of conductivity.

An example of this is supplied by the isomeric methylglucosides,

which do not reduce the conductivity to the same extent; the effect produced by the β -isomeride is uniformly smaller than that produced by the α -compound, although from the change of optical rotatory power it may be inferred that the β -compound unites to a greater extent with the salt than does the α -isomeride.

Although they contain the same number of oxygen atoms in the molecule, the methylglucosides exert a greater influence than glucose itself; this is rather remarkable, seeing that the reducing sugar probably combines more readily with salts than its ethers; possibly in this case the mechanical effect of the non-electrolyte, due to the size of the molecule, comes into play. As indicating a relationship between the magnitude of the molecule and the effect produced, it is interesting to note that the displacement of a hydrogen atom in glucose or cane sugar by the $\cdot\text{C}_6\text{H}_{11}\text{O}_5$ group results in an increase in the reduction of conductivity of about 11.5 per cent. (in solutions containing a gram-molecular proportion of potassium or sodium chloride and 0.5 gram-molecular proportion of sugar in 50 gram-molecular proportions of water).

The reduction of conductivity produced by lactose or melibiose is greater than that effected by cane sugar; possibly the reducing sugars combine with a greater proportion of the salt or as they both crystallise with water, melibiose with two molecules and lactose with one molecule, their greater activity may be due to the withdrawal of a larger proportion of water from the system.

It is clear, therefore, that the results obtained in this investigation do not permit of a simple explanation; they demonstrate, however, the complexity of the changes which accompany the dissolution of substances in water.

XLVIII.—*The Phosphoric Acids.*

By ALFRED HOLT and JAMES ECKERSLEY MYERS.

THE molecular constitution of ortho-, pyro-, and meta-phosphoric acids and the conversion of one into another have been the subjects of many investigations and differences of opinion.

Graham (*Phil. Trans.*, 1833, **52**, 253) by qualitative tests showed the existence of the three varieties of phosphoric acid, and concluded that "the other modifications (meta- and pyro-) pass directly into the condition of this acid (ortho-) on keeping their aqueous solutions for some days or more rapidly on boiling."

Sabatier (*Compt. rend.*, 1888, **106**, 63), by titrating solutions of the meta-acid of different strengths at regular intervals and using

various indicators, concluded that the meta- passes directly into the ortho-variety without the formation of pyro-acid, or at least with the formation of only a trace of it at first, the rate of change being accelerated by concentration and by heat. In further communications (*ibid.*, 1889, **108**, 738, 804), he assumes, with Fleitmann and Henneberg, the existence of complex molecules of the meta-acid, and finds that the rate of change is accelerated by the addition of sulphuric and hydrochloric acids, whilst it is retarded by acetic acid.

Blake (*Amer. Chem. J.*, 1902, **27**, 68), by measurements of the rate of change of the refractive index, concluded that a 10*N*-solution of the meta-acid was completely hydrated in four days.

The results of the investigations of Berthelot and André (*Compt. rend.*, 1896, **123**, 776; 1897, **124**, 265), Giran (*Ann. Chim. Phys.*, 1903, [vii], **30**, 203), and Tanatar (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 99) have been summarised in a paper by Balareff (*Zeitsch. anorg. Chem.*, 1910, **68**, 288), wherein he concludes that their experimental methods, and consequently their conclusion (that pyro-acid is formed as an intermediate substance) are open to criticism. In this paper, Balareff, by an analytical method based on the formation of cadmium or copper pyrophosphate, concludes that the meta-acid passes by hydration directly into the ortho-variety. In a previous paper (*Zeitsch. anorg. Chem.*, 1910, **67**, 234) he showed that whilst at moderate temperatures the dehydration of the ortho-acid produces pyro- and then meta-, at very high temperatures the change from ortho- to meta- should be direct. He did not, however, realise the latter condition experimentally.

Tilden and Barnett (*Trans.*, 1896, **69**, 158) have shown by vapour-density determinations that the molecule of metaphosphoric acid when in the state of vapour is not simple, but is a bimolecular complex, which at a very high temperature shows signs of dissociation. The experiments described at the end of the present communication confirm their observations on the complexity of the molecule.

It appears from the results of the above-mentioned authors that the question of the intermediate formation of pyrophosphoric acid during the hydration of the meta-variety is still unsettled, and, further, that there is uncertainty as to the molecular condition of the three varieties of phosphoric acid in solution.

Our experiments were first directed towards a study of the changes in the depression of the freezing point which a solution of the meta-acid undergoes on keeping, and also the direct estimation of the amount of meta-acid present in such a solution from time to time. Two solutions, the strengths of which were approximately

N- and 2*N*-metaphosphoric acid, were used. The following table gives the depression at varying intervals of time:

TABLE I.

Time (in days).	Depression of f. p.	
	<i>N</i> -Solution.	2 <i>N</i> -Solution.
0	0.697	1.452
2	0.900	1.900
5	1.100	2.465
7	1.203	2.685
10	1.305	2.895
12	1.425	3.150

It will be seen from the above values that the depressions recorded for the 2*N*-solution are slightly more than double those for the *N*-solution, so that it follows, that whatever the nature of the change which is taking place may be, increasing the strength of the solution from *N* to 2*N* does not materially affect the velocity.

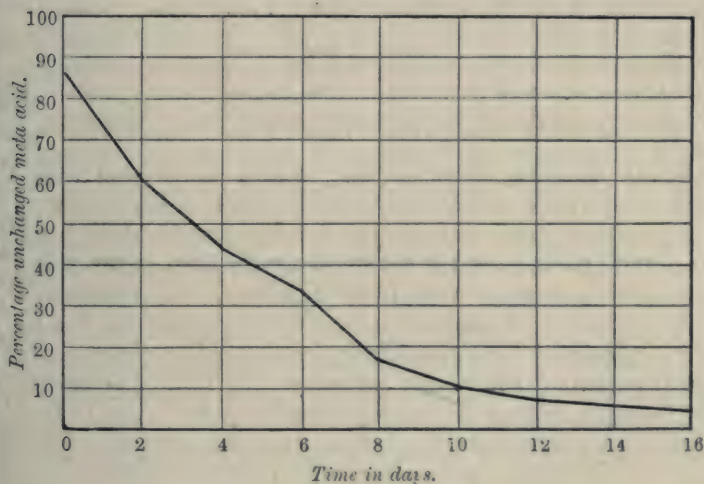
In order to determine the rate at which the hydration took place, the amount of unchanged meta-acid in the solution was estimated from day to day by precipitation with barium chloride. This method was adopted only after numerous trials with other reagents, but preliminary experiments led us to conclude that it was quite trustworthy. When barium chloride is added in large excess to a solution containing ortho-, pyro-, and meta-phosphoric acids, a precipitate is obtained, which, when washed and dried at 100°, was found to have a composition represented by the empirical formula $\text{Ba}(\text{PO}_3)_2$. A large number of samples of this precipitate were prepared and analysed by decomposition with nitric acid, the barium being subsequently estimated as sulphate, and they were found to have a practically constant composition. To test the method still further, a solution of the meta-acid, which had been kept for some time, was precipitated with largely varying amounts of barium chloride, the smallest amount being a slight excess. When the same volumes of the acid solution were taken, the weight of the precipitate obtained did not materially vary. A solution of meta-acid of about normal strength was prepared, and a portion of it precipitated with barium chloride from time to time. The amount of unchanged meta-acid could therefore be calculated, and the values in the following table were obtained:

TABLE II.

Time (hours).	Unchanged meta-acid, per cent.	Unchanged meta-acid in gram-mols.	Water in gram-mols.	K_1 .	K_2 .
0	84.92	0.829	55.53	—	—
46	60.80	0.518	55.22	0.0045	0.0043
99	44.35	0.378	55.08	0.0053	0.0035
142	31.87	0.270	54.97	0.0036	0.0034
190	17.63	0.150	54.85	0.0053	0.0053
238	10.28	0.088	54.79	0.0048	0.0048
287	6.61	0.056	54.76	0.0039	0.0040
382	4.55	0.039	54.74	0.0017	0.0016

The fresh solution contained 0.852 gram-molecule of meta-phosphoric acid, but 15 per cent. of it had changed before the measurements were begun.

An examination of the above table shows, in the first place, that



the values for the percentage of unchanged meta-acid in the solution do not fall on a regular curve, the rate of decrease becoming markedly accelerated after the solution has been kept for about 140 hours. These values are shown for the sake of clearness on the annexed curve. Further, from the values of K_1 and K_2 , which represent the velocities of the reaction calculated for a unimolecular and bimolecular change respectively, it is evident that the hydration of the meta-acid does not take place according to any simple scheme.

As further evidence on this point, the freezing points of a solution of the same strength as that employed for the determination of the meta-acid by precipitation with barium chloride were determined,

and the theoretical values were calculated on the assumption that the acid changed directly into the ortho-variety, dissociation being of a negligible amount. (The latter conclusion is justified by conductivity measurements.)

TABLE III.

Time (hours).	Unchanged HPO_3 in 100 c.c. solution.	Converted HPO_3 calc. as H_3PO_4 in 100 c.c. solution.	A. Depression due to unchanged HPO_3 calc. for simple mols.	B. Depression due to unchanged HPO_3 calc. for double mols.	C. Depression due to unchanged HPO_3 calc. for triple mols.	D. Depression due to changed HPO_3 calc. as H_3PO_4 .	A + D.	B + D.	C + D.	Observed depression.
0	6.64	0.21	1.544	0.772	0.515	0.039	1.583	0.811	0.554	0.697
46	4.14	3.26	0.963	0.481	0.321	0.619	1.582	1.100	0.940	0.900
99	3.02	4.64	0.702	0.351	0.234	0.880	1.582	1.231	1.214	1.040
142	2.17	5.69	0.504	0.252	0.168	1.080	1.584	1.332	1.248	1.170
190	1.20	6.87	0.279	0.139	0.099	1.305	1.584	1.444	1.404	1.240
238	0.70	7.48	0.163	0.081	0.054	1.420	1.583	1.501	1.474	1.305
287	0.45	7.79	0.105	0.052	0.035	1.479	1.584	1.531	1.514	1.420
382	0.31	7.96	0.072	0.036	0.024	1.511	1.583	1.547	1.535	1.500

Table III contains these results. It will be noticed that the freezing point of the almost fresh solution gives a depression corresponding with a molecular weight for the meta-acid of between $(\text{HPO}_3)_2$ and $(\text{HPO}_3)_3$, and it has subsequently been shown that this abnormal value does not arise from ionisation, but is undoubtedly due to the presence of complex molecules. The depression has therefore been calculated for the unchanged meta-acid on the assumption that it is present (a) in simple molecules, (b) in double molecules, and (c) in triple molecules. The experimentally determined values in the last column show that the hydration of the meta-acid does not proceed according to the equation $\text{HPO}_3 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4$, but that at the commencement of the reaction at any rate, the molecules of the meta-acid are complex. From these values it is neither possible to say whether pyro-acid is formed as an intermediate compound, nor whether the complex molecules of the meta-acid first break down and subsequently become hydrated.

Although it has not been found possible to estimate either the pyro- or ortho-acids quantitatively in a mixture of all three varieties, the presence of the pyro-acid has been shown qualitatively by the following method. A solution of the meta-acid which had been kept about a fortnight was neutralised with sodium hydroxide, using phenolphthalein as indicator, and the resulting liquid fractionally precipitated with silver nitrate. At first, the yellow precipitate of silver ortho-phosphate was obtained. This was filtered off, and more

silver nitrate added. By repeating this process, a white precipitate formed, which gradually became yellow. By filtering it off immediately, it was found possible to obtain it absolutely colourless. If the neutralised solution be acidified by a small quantity of dilute nitric acid and then precipitated with silver nitrate, a colourless precipitate is obtained at once, owing to the differing solubility of the silver precipitates in nitric acid.

The white precipitate was washed and dissolved in nitric acid, and the silver precipitated with hydrochloric acid. The resulting acid solution did not coagulate albumen, although a trace of the meta-acid added to it at once brought about this change.

This process was frequently repeated with solutions of metaphosphoric acid which had been kept some time, and always with the same result, so that it must be concluded that the pyro-acid is formed by the action of water on the meta-variety. This confirms the views of Berthelot and André, but is not in accordance with the results of Sabatier and Balareff.

Since orthophosphoric acid on dehydration yields first pyro- and then meta-acid, it follows that on hydration the reverse change should occur. The results of Berthelot and André show that the change from meta- to pyro- proceeds more rapidly than that from pyro- to ortho-, and as the experimental method of Sabatier does not satisfactorily distinguish between pyro- and ortho-acids, the absence of pyro-acid recorded by various authors might arise from one change taking place too fast for observation.

The concentration of the solution will also have its effect. The more dilute it becomes, the faster one would expect the final state to be reached, unless the reaction is truly bimolecular, in which case the greatest velocity would be when the two reacting substances were present in equal concentration. It is therefore possible that the reason we have observed the presence of pyro-acid during the hydration is that our solutions were of a strength particularly favourable to its formation.

From the experiments already described, we were led to examine each of the phosphoric acids separately.

Pure crystalline ortho-acid, when dissolved in water, gave a depression of the freezing point concordant with a molecular weight of 93 (theory 98). Conductivity experiments showed the acid to be very slightly ionised, and it may therefore be concluded that the undissociated molecules in solution are represented by the formula H_3PO_4 .

A few attempts were made to measure the vapour pressure of this acid during dehydration, but the results were inconclusive. Although the pyro- and meta-acids are readily formed from it, no

sudden change in the vapour pressure was detected, such as one would expect when one compound changed into another. It would seem that molecular compounds are probably formed during the dehydration, a conclusion to which Balareff also inclines.

Two varieties of pyrophosphoric acid have been examined. One was a viscid, syrupy liquid obtained by dehydrating the ortho-acid, and the other was obtained in aqueous solution by decomposing lead pyrophosphate by hydrogen sulphide. An approximately normal solution of the syrupy variety gave a depression of the freezing point, which indicated the presence of complex molecules of the acid of composition between $(\text{H}_4\text{P}_2\text{O}_7)_4$ and $(\text{H}_4\text{P}_2\text{O}_7)_5$, whereas in the solution obtained from the lead salt the molecules appeared to be simple. Conductivity measurements again showed little ionisation, so that it may be concluded that very complex molecules, whether associated or not with molecular compounds, are formed by dehydrating the ortho-acid.

The syrupy solution, on keeping for some time, became a mass of crystals, which gave qualitative tests for both ortho- and pyro-acids, so that in this condition the pyro-acid cannot be regarded as a stable substance.

Four varieties of metaphosphoric acid, differing either in physical characters or molecular condition in solution, have been examined. Very little ionisation is found to take place in dilute aqueous solutions, and the differences between them are almost certainly the result of polymerisation into molecules of varying complexity.

The first variety is obtained by heating to redness for a short time sticks of pure glacial phosphoric acid. As thus obtained, it is a vitreous solid, deliquescent in moist air, and readily soluble in water. Freezing-point determinations of its solution indicate the presence of molecules of composition $(\text{HPO}_3)_3$, the values not varying greatly for solutions of strength $2N$ or $N/10$.

When sodium metaphosphate glass is dissolved in water, a depression of the freezing point is obtained, which gives a molecular weight of 314, the theoretical value for $(\text{NaPO}_3)_3$ being 306. It appears therefore that not only the acid, but its alkaline salts, can exist in solution in termolecular complexes.

The second variety is obtained by heating the previous glassy solid to redness for several hours. It is a hard and brittle glass, having a sp. gr. of 2.488. It becomes sticky in moist air, but not so readily as the former variety. When a fragment of this glass is put into water a curious phenomenon, first recorded by Sabatier, takes place. Although a portion seems to dissolve directly, by far the larger amount of the substance is gradually shot off as minute particles into the surrounding water with a sharp, crackling sound,

and the liquid becomes turbid through their presence, solution taking place slowly. When a fragment of this glass is placed in water and viewed microscopically, the particles are seen to be clear fragments with typical glassy fracture. They are expelled with considerable velocity, but as the solution in the immediate neighbourhood of the fragment becomes saturated with the acid, they are formed in constantly decreasing amount.

When this "crackling" variety of the meta-acid is heated for a long time (about twenty-four hours) at a dull red heat, its characters are found to be changed. Although still a hard and brittle glass, its specific gravity has somewhat diminished (2.216), and it is almost insoluble in water. A portion of this glass has been kept in the laboratory for many days without becoming sticky, and when ground to the finest powder takes several days to dissolve in water. No crackling is heard during solution, and no particles are shot off the mass of the glass. Freezing-point determinations show the presence of bimolecular complexes $(\text{HPO}_3)_2$.

When lead metaphosphate is decomposed with hydrogen sulphide, a solution of metaphosphoric acid is obtained, which apparently contains simple molecules of the acid (HPO_3) , since freezing-point determinations give a molecular weight of 102 (theory 80), and the acid is slightly ionised.

These experiments on each of the phosphoric acids show that solutions containing simple molecules can be obtained by decomposing the lead salts, the acids prepared by the dehydration of the ortho-variety invariably containing more or less complex molecules.

The decomposition of a meta- or pyro-salt might be expected to yield simple molecules of the acids, whilst the dehydration of the ortho-acid, since it does not proceed strictly in two stages, would favour the formation of molecular complexes.

The following conclusions may be drawn from the experiments described in this paper:

1. Pyrophosphoric acid is formed as an intermediate compound during the hydration of metaphosphoric acid.

2. The rate of hydration does not accord with any simple order of reaction.

3. Meta- and pyro-phosphoric acids, when prepared by dehydrating the ortho-variety, give complex molecules in solution, but when prepared by decomposing the corresponding lead salts, simpler molecules result.

XLIX.—*The Determination of Solubility Coefficients by Aspiration.*

By WILLIAM JACOB JONES (Fellow of the University of Wales).

It is well-known that a given volume of air aspirated at a sufficiently slow rate through a solution of a gas in a liquid—provided Dalton's law is obeyed—abstracts and carries along with it an amount of the gas which is proportional to the concentration of the solution. Methods based on this fact have been applied to the following problems: (1) to determine the partial pressure of volatile substances in solution (Gahl, *Zeitsch. physikal. Chem.*, 1900, **33**, 178); (2) to compare the relative influence of different salts on the solubility of gases in aqueous solution (McLauchlan, *Zeitsch. physikal. Chem.*, 1903, **44**, 600; Gaus, *Zeitsch. anorg. Chem.*, 1900, **25**, 236; Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 910; Abegg und Riesenfeld, *Zeitsch. physikal. Chem.*, 1902, **40**, 84); (3) to determine the amount of gas in the dissolved state set free in homogeneous equilibria (Jakowkin, *Zeitsch. physikal. Chem.*, 1899, **29**, 626; Orton and Jones, *Trans.*, 1909, **95**, 1456).

On the assumption that the laws of Dalton and Henry hold, a very clear theoretical treatment of the relation between the rates of evasion and of invasion of a gas from and into a liquid respectively, and the solubility of the gas in the liquid, has been given by Bohr (*Ann. Physik*, 1897, [iii], **62**, 644; 1899, **68**, 500). He experimented with solutions of carbon dioxide in water and in sodium chloride solutions. He considers that when a rapid current of an inert gas free from carbon dioxide is passed over a well-stirred solution of carbon dioxide, the time-rate of escape (or "evasion") of the latter gas from solution is proportional to the concentration of the solution and to its exposed surface. From the mathematical expression of this assumption he obtains an "evasion coefficient," β , which denotes the volume of carbon dioxide (at N.T.P.) escaping per minute through 1 sq. cm. of exposed surface, into an atmosphere free from that gas, from a solution containing 1 c.c. (at N.T.P.) in 1 c.c. of the solution. In a similar way he defines the "invasion coefficient," γ , of carbon dioxide into water as the volume of that gas which, under a pressure of 760 mm. of mercury, enters through 1 sq. cm. of surface per minute into well-stirred water free from carbon dioxide. If α denotes the absorption coefficient of carbon dioxide in water, it is easily seen that $\gamma = \alpha\beta$. Bohr determined α by abstracting the gas from its saturated solution by means of a Hagen pump, and measuring the volume of gas. He determined γ

both experimentally and by substituting the values he had found for α and β in this formula. The comparison does not show a very good agreement between the calculated and found values of γ .

Perman has made very extensive use of aspiration methods of experiment, applying them to the following determinations: (1) the rate of escape of ammonia from the aqueous solution when a uniform current of air is bubbled through it (Trans., 1895, **67**, 868, 983; 1898, **73**, 511)—he shows that the amount of ammonia, q , present in the solution when a volume, V , of air has been drawn through is represented by the equation $\log q = a + b.V$, a and b being constants for a given experiment; (2) the vapour pressure of water and the partial pressure of ammonia in its aqueous solutions (Trans., 1901, **79**, 718; 1903, **83**, 1168; *Proc. Roy. Soc.*, 1903, **72**, 72). He has also made a careful study of the sources of error of the method (*J. Physical Chem.*, 1905, **9**, 36; *Proc. Roy. Soc.*, 1905, **76**, A, 174).

Steele (Trans., 1903, **83**, 1470) assumes that "the desaturation of a saturated solution of hydrogen chloride in toluene by a steady current of hydrogen follows the course of a unimolecular reaction, namely:

$$K = \frac{1}{T} \log_e \frac{a}{a-x},$$

where a denotes the amount of gas contained in the saturated solution, and x the amount carried away in the time T ."

When the molecular condition of a substance is the same in two phases, it divides itself between them, so that the ratio of its concentration in one phase to its concentration in the other phase is always a constant (the Partition Law). On this law as basis, Ostwald defines the solubility coefficient of a gas in a liquid as the ratio, when equilibrium has been established, of the concentration of the gaseous solute (in gram-molecules per unit volume) in the liquid phase to its concentration in the vapour phase in contact with the former phase; otherwise expressed:

$$\text{Solubility coefficient} = \frac{\text{Concentration in the liquid phase}}{\text{Concentration in the vapour phase}}.$$

In this paper it is shown that solubility coefficients of volatile solutes, provided the system obeys the laws of Dalton and Henry, can be determined from the amount of solute which is carried away by an inert gas when known volumes are bubbled through solutions of known strength and volume.

Let a volume V c.c. of an inert gas be drawn at a very slow rate and in very minute bubbles through a volume v c.c. of a well-stirred solution of a volatile substance maintained at a constant temperature; if s denote the solubility coefficient, a the amount of

volatile solute initially, and b the amount finally, present in the solution, then it can be shown that

$$s = \frac{V}{v \cdot \log_e \frac{a}{b}}.$$

Evidently $(a-b)$ denotes the amount of solute abstracted by the inert gas.

In order to establish this relation, consider an instant when a volume x c.c. of inert gas has been bubbled through. At this instant let the amount of volatile solute in the solution be y gram or y gram-molecules; let a small additional volume δx of inert gas be drawn through, and let it abstract a small amount δy of solute from the solution. Then, provided the solution is well stirred and the inert gas is in the form of very small bubbles and drawn through at such a rate that the solute is allowed sufficient time to attain at each instant its maximum partial pressure in the abstracting gas (which takes the less time to accomplish the more minute the bubbles), it follows from the definition that

$$s = \frac{\frac{y}{v}}{\frac{\delta y}{\delta x}},$$

and, in the limit,

$$\frac{dy}{dx} = \frac{y}{v \cdot s}.$$

Since, as x increases, y diminishes, we may change the sign of the right-hand side, and on integration between the limits, $x=0$, $y=a$ and $x=V$, $y=b$, we obtain:

$$s = \frac{V}{v \cdot \log_e \frac{a}{b}}.$$

From this equation, we can at once draw the following deductions:

(1) When such a small volume of abstracting gas is employed that only a small quantity of solute is removed, s is given by the obvious relation (Jakowkin, *loc. cit.*):

$$\frac{1}{s} = \frac{\frac{(a-b)}{V}}{\frac{a}{v}},$$

for:

$$\frac{1}{s} = \frac{v}{V} \cdot \log_e \frac{a}{b} = \frac{v}{V} \cdot \log_e \left(1 + \frac{a-b}{b} \right).$$

On expanding the logarithm factor in series, and neglecting the

square and higher powers of the small quantity $(a-b)/b$, we obtain:

$$\frac{1}{s} = \frac{v \cdot (a-b)}{V \cdot b} = \frac{v \cdot (a-b)}{V \cdot a}$$

approximately.

(2) The logarithmic law found empirically by Perman (*loc. cit.*) for the rate of loss of ammonia by a solution through which a steady current of air is being aspirated follows thus:

$$\log a - \log b = \frac{V}{s \cdot v}.$$

In a given experiment, s , v , and $\log a$ are all constant, and b denotes the amount of gas in solution after a volume V of air has been bubbled through:

$$\therefore \log b = - \frac{V}{s \cdot v} + \log a$$

(compare Perman, *loc. cit.*)

$$\log q = b \cdot V + a.$$

(3) An explanation of the direct proportionality between the amount of solute carried away by a given volume of abstracting gas and the strength of the solution (Orton and Jones, *loc. cit.*, p. 1463) is furnished by this equation, for in such a series of experiments,

$$v_1 = v_2 = v_3 = \dots; \text{ and } V_1 = V_2 = V_3 = \dots$$

Whence

$$\log \frac{a_1}{b_1} = \log \frac{a_2}{b_2} = \dots$$

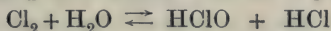
$$\therefore \frac{a_1}{b_1} = \frac{a_2}{b_2} = \dots$$

and

$$\frac{a_1 - b_1}{a_1} = \frac{a_2 - b_2}{a_2} = \dots$$

that is, the amount of solute carried away by the inert gas is proportional to the initial concentration of the solution (see Fig. 3).

This relation affords a means of testing whether the volatile solute-solvent system obeys the laws of Dalton and Henry or not. For this purpose a number of experiments are carried out, using solutions varying in strength from the most dilute up to the saturated solution. If this proportionality holds throughout that range, then these laws are followed. By this means it was found that defection arose in the case of dilute chlorine solutions in water, showing clearly the existence of the equilibrium:



investigated by Jakowkin (*loc. cit.*) (see table VI and Fig. 2).

The value of

$$\frac{V}{v \log_e \frac{a}{b}},$$

which, if this equilibrium did not exist, would be constant, increases with dilution.

In the case of bromine water, the corresponding formation of hypobromous acid and hydrobromic acid is very much less extensive (see table IX) (compare Bray, *J. Amer. Soc.*, 1910, **32**, 932).

Provided an accurate knowledge of each of the quantities, a , b , V , and v , is possible, the formula:

$$s = \frac{V}{v \cdot \log_e \frac{a}{b}}$$

furnishes a means of experimentally determining solubility coefficients. In the following section it is shown how this can be accomplished. It is more practicable to take for the value of b the difference between the value of a , which is accurately determined, and the amount of solute which is carried away by the abstracting gas—this being trapped by suitable means and accurately estimated—than by direct estimation. The accurate value obtained in this way is roughly checked by the analysis of an aliquot portion of the solution at the end of the aspiration.

It will be noticed that the solubility coefficient can be determined by this method without the necessity of preparing a saturated solution.

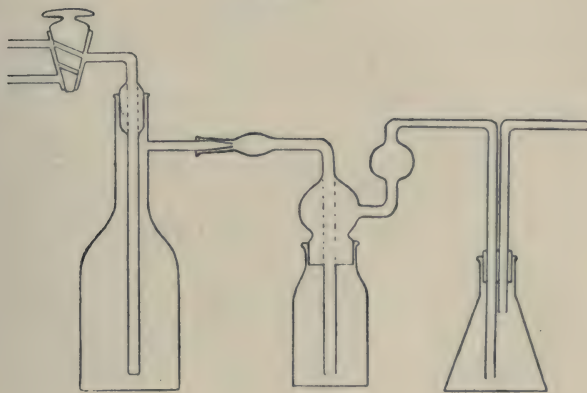
EXPERIMENTAL.

Experiments in verification of the preceding theorem were carried out with chlorine and bromine solutions in carbon tetrachloride, in acetic anhydride, in acetic acid, in water, and in aqueous acetic acid.

The apparatus consisted of a bubbler containing the solution, followed by small wash-bottles containing potassium iodide solution, and finally the aspirator, the whole being immersed in a constant temperature bath. The bubbler and the potassium iodide wash-bottles are shown in Fig. 1. They were designed by Professor Orton. The leading tubes were of capillary tubing, and passed through a solid glass stopper. By this means the waste dead space above the solution was reduced to a minimum, the bubbler being as nearly as possible full of solution. On the tube connecting this vessel with the first potassium iodide wash-bottle, a small bulb had been blown, and this was packed with glass-wool, which, experiment showed, completely removed all spray from the air. This

potassium iodide wash-bottle was attached by means of a well-ground glass joint. It was followed by a second wash-bottle, also containing potassium iodide solution; this, however, was not necessary except where the halogen solution was very concentrated, absorption being complete in the first wash-bottle. Titration of the iodine set free in these wash-bottles gives the amount of chlorine or bromine carried away by the air ($=[a-b]$). The solutions were prepared from dry chlorine and bromine in glass-stoppered vessels, and transferred, without exposure to the air, to a standard burette, from which a portion of the solution was delivered into potassium iodide solution and a known volume (v c.c.) poured into the bubbler so as to fill it as completely as possible. Titration of the iodine set free from the potassium iodide served to give the amount (a) of

FIG. 1.



halogen introduced into the bubbler. It was found that with care the loss of chlorine and bromine during this transference was very small, and it is doubtful whether a greater accuracy could have been attained by preparing the solutions *in situ* in the bubbler. In some of the later experiments (tables IV, V, VI, IX, XII), a was determined in a different way, thus: a known volume of solution was introduced into the bubbler, and by means of a standard pipette, 2 c.c. of the solution were withdrawn and poured into potassium iodide solution. When the solution had acquired the temperature of the bath, a current of air, freed from dust and water vapour, saturated with the vapour of the solvent, and maintained at the temperature of the experiment by being drawn through the apparatus in the bath, was bubbled through the solution. Efficient stirring was ensured by the narrow form of the bubbler and the minuteness of the bubbles. Trials showed that

under the conditions of the experiments there was no difference in the amount of chlorine carried over when 250 c.c. of air were bubbled through in times varying from one and a-quarter to fifty-one minutes. The volume (V) of air aspirated through the solution was determined by measuring the volume of liquid displaced in the aspirator by syphoning it over into graduated flasks. In experiments of accuracy, in order to ensure that the air measured in the aspirator was as nearly as possible under the same conditions—especially as regards volume—as the air aspirated through the solution, it would be necessary to fix a calcium chloride drying-tube following the last potassium iodide wash-bottle in order to remove the aqueous vapour and to fill the aspirator with the pure solvent, thereby reducing the air to exactly the same condition as it was in when passing through the solution. For the same reason it is necessary that the air should not at any time during its passage through the apparatus bubble through any considerable depth of liquid between the bubbler and the aspirator, which for this purpose should be as squat in form as possible. The air, which passes through the solution in the form of spherical bubbles, is collected in the aspirator above the plane surface of the liquid. Now the pressure inside a spherical bubble of radius r exceeds the pressure outside by $2T/r$, where T denotes the surface tension. Hence, in order to avoid having to make a correction owing to surface tension, it is necessary that the bubbles should not be too minute. The total error in the measurement of V , made by assuming the volume of liquid syphoned from the aspirator to be equal to the sum of the volumes of the bubbles of air as they passed through the solution, in consequence of these sources of error was less than 0.2 c.c. per 100 c.c.

Titration of iodine set free were carried out with $N/50$ -sodium thiosulphate solution delivered from a standard 10 c.c. burette graduated in 0.02 c.c. In the tables the titres have been reduced to $N/10$.

The solutions were shielded from light, and the experiments were carried out in a darkened room.

Special attention was given to the purity of all chemicals used. The specially purified acetic acid was partly prepared in this laboratory, and partly obtained from Kahlbaum. The carbon tetrachloride was redistilled several times. The bromine was washed with water, dried with sulphuric acid, and distilled from a few crystals of potassium bromide. Kahlbaum's acetic anhydride was used without further purification.

By the term "75 per cent. acetic acid" is meant a solution prepared by mixing 75 volumes of glacial acetic acid with 25 volumes

of pure redistilled water, and similarly with acetic acids of other concentrations.

TABLE I.

Chlorine in Carbon Tetrachloride. Temperature 15°.

v.	V.	Time occupied in aspiration, minutes.	(a - b).	a.	b.		s.
					Calc.	Found.	
95.0	436.0	13	3.85	47.01	43.16	42.92	53.7
95.0	430.0	5	3.22	38.27	35.05	35.00	51.4
95.0	297.0	3	3.93	65.55	61.62	61.05	51.0
95.0	298.0	4	0.75	12.55	11.80	11.57	50.7
							51.7

TABLE II.

Chlorine in 99.84 per cent. [0.16 per cent. water] Acetic Acid.
Temperature 16°.

95.0	250.0	2.5	3.68	53.30	49.62	49.20	36.9
95.0	250.0	2.5	1.99	28.70	26.71	26.50	36.6
95.0	250.0	2.5	5.10	73.00	67.90	66.80	36.4
95.0	250.0	3.3	2.18	31.70	29.52	29.32	36.9
							36.7

TABLE III.

Chlorine in 90 per cent. Aqueous Acetic Acid. Temperature 15°.

95.0	250.0	2.5	2.53	26.41	23.88	—	26.1
95.0	250.0	2.5	12.83	128.8	116.0	—	25.1
95.0	250.0	2.5	6.04	59.09	53.05	—	24.4
95.0	250.0	2.5	2.41	24.40	22.0	—	25.4
							25.3

TABLE IV.

Chlorine in 75 per cent. Aqueous Acetic Acid. Temperature 15°.

v.	V.	Time occupied in aspiration, minutes.	(a - b).	a.	s.
104.0	250.0	4.8	3.322	24.34	16.39
104.0	250.0	5.0	8.664	63.42	16.39
104.0	250.0	4.8	10.790	79.57	16.50
					16.43

TABLE V.

Chlorine in 65 per cent. Aqueous Acetic Acid. Temperature 15°.

104.0	250.0	4.8	3.994	25.06	13.83
104.0	250.0	4.5	6.620	39.54	13.10
104.0	250.0	4.5	14.04	85.30	13.36
					13.43

TABLE VI (see Fig. 2).
Chlorine in Water. Temperature 15°.

<i>v.</i>	<i>V.</i>	Time occupied in aspiration, minutes.	<i>(a - b).</i>	<i>a.</i>	<i>V</i>	
					<i>v. log</i>	$\frac{a}{b}$
104.0	100.0	7.0	33.44	250.3	6.7	
104.0	100.0	7.0	20.65	177.5	7.7	
104.0	100.0	7.0	11.92	136.0	8.4	
104.0	100.0	7.0	11.19	112.1	9.1	
104.0	100.0	7.0	9.687	110.4	10.4	
104.0	100.0	7.0	6.146	76.78	11.5	
104.0	105.9	7.3	1.199	28.66	22.5	
104.0	100.0	7.0	0.514	19.21	35.5	
104.0	100.0	7.0	0.0077	4.207	524.8	

FIG. 2 (see Table VI).

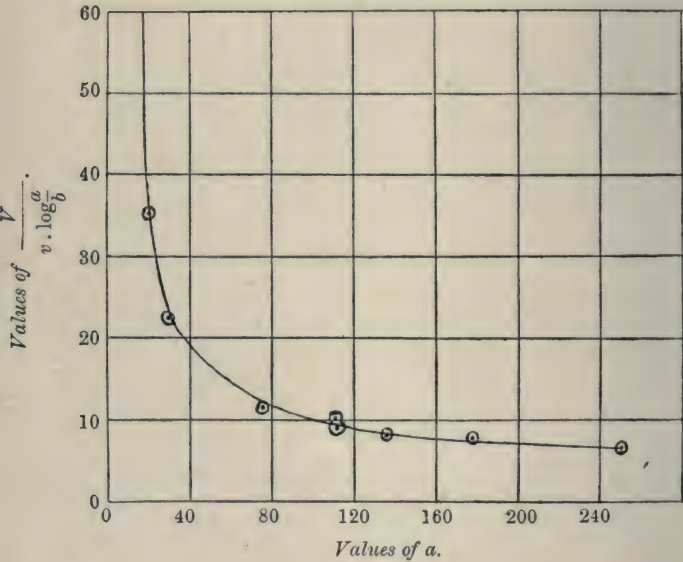


TABLE VII.

Bromine in 90 per cent. Aqueous Acetic Acid. Temperature 15°.

<i>v.</i>	<i>V.</i>	Time occupied in aspiration, minutes.	<i>(a - b).</i>	<i>a.</i>	<i>b.</i>		<i>s.</i>
					Calc.	Found.	
95.0	1000	30	3.02	157.32	154.30	154.0	543
95.0	1000	10	1.23	64.60	63.37	62.96	561
95.0	1000	10	1.19	64.03	62.84	62.63	538
95.0	1000	10	2.05	105.72	103.67	103.15	560

TABLE VIII.

Bromine in 25 per cent. Aqueous Acetic Acid. Temperature 15°.

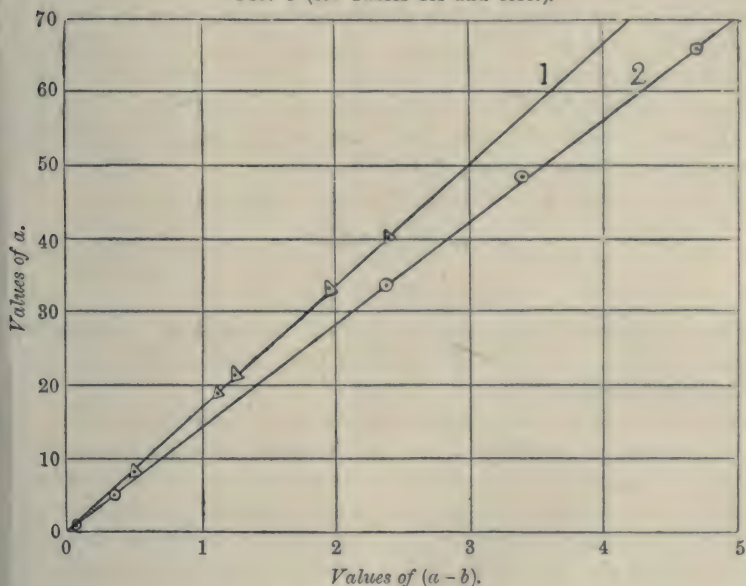
104	500	12	5.88	68.70	62.82	62.92	54
104	500	12	2.78	34.35	31.57	31.20	57
							56

TABLE IX (see Curve 2, Fig. 3).

Bromine in Water. Temperature 15°.

<i>v.</i>	<i>V.</i>	Time occupied in aspiration, minutes. (<i>a</i> - <i>b</i>).		<i>a.</i>	<i>s.</i>
104.0	500	12	9.17	66.37	32.3
104.0	250	6	4.70	65.97	32.5
104.0	250	10	3.382	48.63	33.4
104.0	250	6	2.30	33.00	33.2
104.0	250	10	0.357	5.211	33.9
104.0	250	10	0.075	1.267	39.4

FIG. 3 (see Tables IX and XII.).



When *s* has been determined by experiments similar to the preceding for a given volatile substance in a medium, the concentration of the volatile substance existing in the free state in solution in homogeneous equilibria in the medium may be determined by aspiration experiments, for

$$\log_e \frac{a}{b} = \frac{V}{v \cdot s} \dots \dots \dots (1)$$

and $a - b$ = amount of volatile solute carried over by V c.c. of inert gas from v c.c. of solution (2).

Solving these two equations, we obtain a , the concentration of the dissolved volatile substance. In order to disturb the equilibrium as little as possible, it is essential that the amount of solute extracted from the solution by the inert gas should be no more than is necessary for accurate analysis.

As an illustration of this application may be given the following investigation of the extent of combination of bromine and hydrogen bromide in water, in acetic acid, and in aqueous acetic acids. A considerable amount of work has been done on this subject in aqueous solution, both by methods based on extraction of the bromine by means of such liquids as carbon disulphide and carbon tetrachloride (Wildermann, *Zeitsch. physikal. Chem.*, 1893, **11**, 407; Roloff, *ibid.*, 1894, **13**, 341; Jakowkin, *ibid.*, 1896, **20**, 19), and by electrolytic methods (Boericke, *Zeitsch. Elektrochem.*, 1905, **11**, 57). Measurements of velocities of bromination in aqueous solution always reveal an apparent loss of activity on the part of bromine with the progress of the reaction. This is due to the combination of the hydrogen bromide produced with the bromine to form hydrogen tribromide (Ramberg, *Zeitsch. physikal. Chem.*, 1900, **34**, 561; Bruner, *ibid.*, 1902, **41**, 513; Bugarszky, *ibid.*, 1901, **38**, 561; 1904, **48**, 63; Bognár, *ibid.*, 1910, **71**, 529).

Bugarszky shows how the equilibrium constant:

$$K = \frac{[\text{HBr}][\text{Br}_2]}{[\text{HBr}_3]}$$

$$\text{HBr} + \text{Br}_2 \rightleftharpoons \text{HBr}_3$$

may be calculated from measurements of the speed of bromination of acetaldehyde. At 25° he obtains the value 0.0665 for K ; Jakowkin's value is 0.065.

The procedure in the present experiments was as follows. A known volume of standard hydrogen bromide solution was put in a flask in the bath. A solution of bromine in the solvent was standardised, and a known volume run in from a burette into the bubbler. So much solvent was added to the hydrogen bromide solution, that on mixing with the bromine solution a convenient volume of solution was obtained. When the solutions had acquired the temperature of the bath, the contents of the flask were poured into the bubbler, and the whole having been allowed to stand in order that equilibrium should be established, a known volume of air was aspirated through. By substituting the value of the amount of bromine carried over by the air in equation (2), the two equations on solution give the value of a , for example, the concentration of Br_2 in the system.

As examples may be given the following two experiments:

TABLE X.

Medium.	50 per cent. acetic acid.	Water.
v	104	104
V	500	250
Amount of Br_2 used in preparation per litre of solution, gram-mol.	0.0330	0.0316
Amount of HBr used in preparation per litre of solution, gram-mol.	0.0330	0.0316
Time which elapsed between mixing and beginning of aspiration (minutes)	10	12
Time occupied in aspiration (minutes)	13	6
Titre of 10 c.c. solution at the end of the aspiration	6.531	5.950
Titre of Br_2 carried away by air	1.130,	3.335,
corresponding with a concentration of Br_2 (and HBr)	0.0172	0.0230
concentration HBr_2	0.0158	0.0086
Value of K	0.0187	0.061

TABLE XI.

Medium.	Tempera- ture.	Gram-mols. used in preparation of 1 litre of solution.		Gram-mols. per litre in equilibrium.			K .
		Br' .	Br_2 .	Br_3' .	Br_2 .	Br' .	
Water.	{ 15	0.0316	0.0316	0.0086	0.0230	0.0230	0.061
	{ 15	0.0158	0.0158	0.0028	0.0130	0.0130	0.061
	{ 15	0.0316	0.0316	0.0088	0.0228	0.0228	0.059
25 per cent. aqueous acetic acid.	{ 15	0.0330	0.0330	0.0145	0.0185	0.0185	0.024
50 per cent. aqueous acetic acid.	{ 15	0.0100	0.0070	0.0020	0.0050	0.0080	0.020
	{ 15	0.0330	0.0330	0.0158	0.0172	0.0172	0.019
	{ 16	0.0200	0.0200	0.0151	0.0049	0.0049	0.0016
99.6 per cent. acetic acid.	{ 16	0.0400	0.0400	0.0290	0.0110	0.0110	0.0042
	{ 16	0.0216	0.0122	0.0080	0.0042	0.0136	0.0071
	{ 16	0.0225	0.0251	0.0142	0.0109	0.0083	0.0064
	{ 16	0.1160	0.0959	0.0830	0.0129	0.0330	0.0051

Jakowkin obtained the value 0.065 for K for aqueous solutions at 25° .

The value of K increases with increasing dilution of the acetic acid, showing that the formation of perbromides is more extensive in concentrated acetic acid than in dilute acetic acid. The inconstancy in the value of K in glacial acetic acid solution may be due to incomplete ionisation of the tribromide or to an appreciable formation of higher perbromides. Steiner (*Ber.*, 1874, **7**, 184), by the employment of low temperatures, isolated acetic acid hydrobromide perbromide from mixtures of bromine, hydrogen bromide, and glacial acetic acid, and, unless this compound undergoes complete thermal dissociation at 16° , it must interfere with the equilibrium.

In sharp contrast to the behaviour of bromine and hydrogen bromide, chlorine and hydrogen chloride do not combine to any appreciable extent. With as much as eight equivalents of hydrogen chloride to one of chlorine in glacial acetic acid solution, all the chlorine was found to be free. Table XII shows some similar experiments made with acetic anhydride solutions.

TABLE XII (see Curve 1, Fig. 3).

Chlorine in Acetic Anhydride. Temperature 15°.

v.	V.	Time occupied in aspiration (minutes).	Gram-mols. used in preparation per litre of solution.		Amount of chlorine expressed as the titre of 104 c.c. solution in c.c. <i>N</i> /10.		
			Hydrogen chloride.	Chlorine.	<i>a</i> .	(<i>a</i> - <i>b</i>).	<i>s</i> .
104·0	250·0	10	0·0000	0·01574	32·75	1·943	39·6
104·0	250·0	10	0·0000	0·01015	21·10	1·229	40·1
104·0	250·0	10	0·0000	0·00403	8·390	0·503	38·8
104·0	250·0	10	0·0293	0·01925	40·04	2·400	39·0
104·0	250·0	10	0·0353	0·00916	19·05	1·165	38·6

The author is greatly indebted to Professor Orton, who suggested this investigation, for the interest he has taken therein, and for his kind help in designing the apparatus.

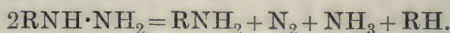
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BANGOR.

L.—*The Auto-reduction of Hydrazines.*

By FREDERICK DANIEL CHATTAWAY and MONTAGUE ALDRIDGE.

AROMATIC hydrazines, when heated, undergo simultaneous oxidation and reduction. As the precise course of any such auto-reduction depends only on the group to which the hydrazine concerned belongs, these interactions may be expressed by general equations.

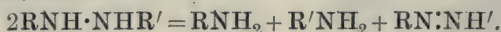
Primary hydrazines yield a primary amine, nitrogen, ammonia, and a hydrocarbon, thus:



Unsymmetrical secondary hydrazines yield a secondary amine, nitrogen, and ammonia, thus:



Symmetrical secondary hydrazines yield a primary amine and an azo-compound, thus:



Many of these reactions go on slowly even at the ordinary temperature, the rate increasing rapidly as the boiling point of the hydrazine is approached. It is thus impossible to obtain any aromatic hydrazine quite pure by distillation, or to keep it so for an unlimited time, even when air is excluded.

When the hydrazines contain only unsubstituted hydrocarbon residues, the reactions are, as a rule, quantitative, but in the case of hydrazines containing substituted aromatic residues, although these primary decompositions take place to a considerable extent, other secondary reactions may also occur, especially at a high temperature, due to the presence of the substituted atoms or groups.

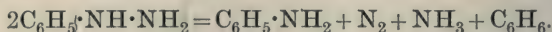
Action of Heat on Phenylhydrazine.

Emil Fischer, in his well-known paper describing the compound (*Annalen*, 1878, **190**, 81), noted that when phenylhydrazine was distilled under the ordinary pressure, a small quantity of ammonia was liberated. This he removed by exposing the freshly distilled liquid in a vacuum over sulphuric acid, but some years afterwards (*Annalen*, 1886, **236**, 198) he recommended that it should be distilled under diminished pressure to avoid this decomposition. Evidently this procedure, also, did not prove entirely satisfactory, for he later stated (*Ber.*, 1893, **26**, 19) that it is best obtained quite pure by frequently freezing it out from double its volume of ether at -10° . Walter (*J. pr. Chem.*, 1896, [ii], **53**, 471) observed that phenylhydrazine, when heated in a sealed tube to 300° for three to four hours, decomposed into aniline, nitrogen, ammonia, and benzene, and Struthers (*Proc.*, 1905, **21**, 95) discovered that this action took place with almost explosive violence when small quantities of cuprous cyanide or cobalt cyanide were added to phenylhydrazine heated to near its boiling point.

It has, however, never been recognised that this reaction proceeds comparatively rapidly when phenylhydrazine is boiled, and that the liberation of ammonia which occurs when it is distilled is accompanied by the continuous evolution of nitrogen and formation of aniline, and, moreover, that the reaction is a characteristic general one of all primary aromatic hydrazines.

To investigate the reaction, 150 grams of pure phenylhydrazine, recently distilled under a pressure of 20 mm. and boiling constantly, were placed in a small, round-bottomed flask connected with a reversed condenser, through which steam was passed. The upper end of this was attached to a short upright condenser dipping into a flask, and the latter to a Volhard trap containing dilute hydrochloric acid. The exit tube from the trap dipped below the surface of water in a small pneumatic trough. The air contained in the

apparatus having been displaced by hydrogen, the phenylhydrazine was heated to gentle ebullition for about twelve hours. At first it boiled quietly at 241° . Ammonia and nitrogen were continually evolved, whilst benzene, which escaped condensation in the heated condenser, collected in the flask attached to the cooled condenser. After twelve hours' boiling, the residue in the flask was distilled and found to consist practically entirely of aniline. The nitrogen escaping was measured, and the ammonia weighed as ammonium chloride. The decomposition was thus shown to take place, within the limits of experimental error, quantitatively according to the equation:

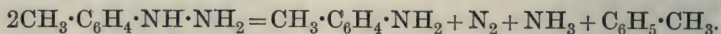


This auto-reduction of phenylhydrazine takes place completely and instantaneously if the vapour of the compound is passed through a short length of hard glass tube packed with porous porcelain, and heated to a dull red heat in a furnace. The products are the same as when the decomposition is effected at the boiling temperature. Ammonia and nitrogen are liberated, whilst a mixture of aniline and benzene condenses. Small quantities of compounds boiling at a temperature higher than the boiling point of aniline are also present in the liquid condensing, formed doubtless by the action of heat on the benzene and aniline.

Action of Heat on the Tolyhydrazines.

Fifty grams of *p*-tolylhydrazine were heated in the apparatus previously described, but with the steam-heated condenser replaced by a thin-walled glass tube filled with beads, and of such a length that when the liquid was gently boiling, only the toluene produced passed over into the second condenser.

p-Tolylhydrazine undergoes auto-reduction more easily than does phenylhydrazine, but in an exactly similar manner. It decomposes quantitatively into *p*-toluidine, nitrogen, ammonia, and toluene, thus:

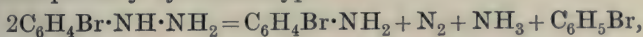


o-Tolylhydrazine behaves similarly to the *p*-compound, and yields *o*-toluidine, nitrogen, ammonia, and toluene.

Action of Heat on p-Bromophenylhydrazine.

p-Bromophenylhydrazine at an elevated temperature decomposes much more easily than the unsubstituted phenylhydrazine. When heated above its melting point, bubbles of gas are given off between 115° and 120° . At about 140° the gas evolution becomes rapid,

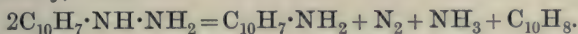
nitrogen, ammonia, and bromobenzene are set free, and so much heat is evolved that even if the flame is removed the temperature quickly rises to about 210° , the action becoming violent. A brownish-black residue, which dissolves in alcohol to a blue liquid, is left in the distilling flask. On distilling, it yields considerable quantities of bromobenzene and *p*-bromoaniline. The main decomposition is of the usual primary hydrazine type:



but other subsidiary reactions take place to a small extent.

Action of Heat on the Naphthylhydrazines.

When α -naphthylhydrazine is heated above its melting point, bubbles of nitrogen and a little ammonia are given off at about 120° . As the temperature is raised, the evolution of gas increases, until at about 240 — 260° it is very vigorous, ammonia and nitrogen being rapidly liberated, whilst naphthalene is set free. On distilling the solid residue, it is found to consist of a mixture of α -naphthylamine and naphthalene. The decomposition takes place quantitatively, thus:



β -Naphthylhydrazine decomposes similarly, but more easily. The liberation of ammonia is noticeable even at 60° , and at 120° bubbles of nitrogen form rapidly in the melted mass. The decomposition becomes, as before, more vigorous as the temperature rises to 250° . On distilling the residue after the evolution of gas has ceased, it is found to consist of β -naphthylamine and naphthalene.

Auto-reduction of the naphthylhydrazines goes on to an appreciable extent at the ordinary temperature, and naphthalene and ammonia can be recognised by their odour in any specimen of a naphthylhydrazine which has been kept for a long time.

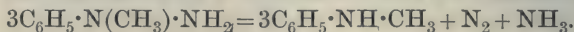
Action of Heat on as-Diphenylhydrazine.

as-Diphenylhydrazine gave off a little ammonia when melting, but no noticeable evolution of gas occurred until about 260 — 270° , when nitrogen and ammonia were rapidly evolved and so much heat liberated that action continued after the withdrawal of the flame. After heating some time to 287 — 288° , evolution of gas ceased, and the residue proved, on distillation, to be practically pure diphenylamine, only a little black tar being left behind in the distilling flask. No diphenyl could be recognised. The action was found to proceed practically quantitatively according to the equation:

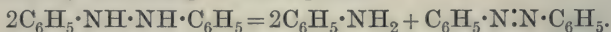


Action of Heat on as-Phenylmethylhydrazine.

Fifteen grams of *as*-phenylmethylhydrazine were made to boil gently for about eight hours in the apparatus previously described, the air having been displaced as before by hydrogen. Nitrogen and ammonia were continuously evolved. When evolution of gas had ceased, the residue in the flask was distilled, and found to consist of methylaniline. The action is thus similar to that which takes place when *as*-diphenylhydrazine is heated, and may be represented thus:

*Action of Heat on s-Diphenylhydrazine.*

It has long been known that the hydrazo-compounds, when heated alone, decompose into azo-derivatives and anilines. This was first noted by Hofmann (*Proc. Roy. Soc.*, 1863, **12**, 577) in the paper in which he described the discovery of hydrazobenzene. When hydrazobenzene is heated to about 200°, auto-reduction begins, with so considerable an evolution of heat that if more than a few grams be taken, the reaction proceeds to completion, even if the flame is withdrawn. The product then distils between 210° and 225°, the bulb of the thermometer being immersed in the liquid. The distillate is a red oil, from which azobenzene crystallises on cooling. It consists solely of aniline and azobenzene, the reaction proceeding quantitatively according to the equation:



The *s*-ditolylhydrazines behave exactly similarly on heating, whilst monoacetylhydrazobenzene yields aniline, acetanilide, and azobenzene. The reaction therefore is a general one.

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OXFORD.

LI.—*A Synthesis of Derivatives of Phenothioxin.*

By THOMAS PERCY HILDITCH and SAMUEL SMILES.

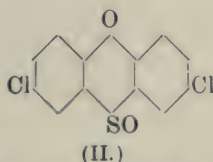
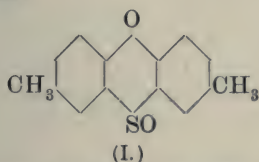
DURING the investigation of certain aromatic hydroxysulphoxides (Gazdar and Smiles, *Trans.*, 1910, **97**, 2248), attempts were made to obtain triarylsulphonium bases from them by condensation with a phenolic ether in presence of concentrated sulphuric acid, but the desired result was not obtained. The negative results obtained with these sulphoxides of *p*-cresol and *p*-chlorophenol seemed

remarkable, for the corresponding ethers, *p*-cresetole and *p*-chlorophenetoles sulphoxides, condense readily under the stated conditions, giving good yields of the aromatic sulphonium salt (compare Smiles and Le Rossignol, *Trans.*, 1908, **93**, 709).

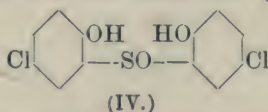
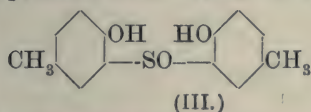
The experiments described in this paper were undertaken with the object of ascertaining the cause of the inactivity of these hydroxy-sulphoxides.

The preparation of the latter substances and their chief derivatives has been described in the previous paper (Gazdar and Smiles, *loc. cit.*). In that place, attention was drawn to the fact that all the hydroxy- or alkyloxy-sulphoxides hitherto prepared furnish intensely coloured solutions with concentrated sulphuric acid, and that it is probably the nature of the substances then formed which determines the reactivity of the sulphoxides in this solvent.

It has now been found that the moderately prolonged action of sulphuric acid on the sulphoxides of *p*-cresol and *p*-chlorophenol yields the phenothioxin oxides represented by the following formulæ:



Taking first the dimethyl compound, it is evident that the sulphoxide from which it is prepared has the structure (III),

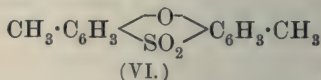
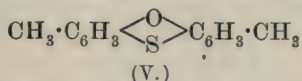


for the dimethyl ether obtained from it by methylation is identical with the di-*p*-cresol methyl ether sulphoxide which has been previously shown to have this structure (Le Rossignol and Smiles, *Trans.*, *loc. cit.*). The constitution which is now ascribed to the product obtained from this sulphoxide by the interaction with sulphuric acid is shown by the facts:

1. It is produced by loss of the elements of water from the hydroxy-sulphoxide.
2. When reduced, it loses one atomic proportion of oxygen, and
3. When oxidised, it absorbs the same quantity of that element.
4. Neither the substance itself, nor the products of its oxidation or reduction, contain hydroxyl.

It may also be observed that the molecular weight of the reduction product corresponds with this structure.

From this constitution of the substance, those of the reduction and oxidation products follow; these are respectively the phenothioxin itself (V) and the phenothioxin dioxide (VI):



The constitution of the dichloro-compound cannot be said to be based on such rigid proof as that of the dimethyl derivative, for the structure of the *p*-chlorophenol sulphoxide has not been so definitely established. But the product obtained by the action of sulphuric acid with this sulphoxide so closely resembles dimethylphenothioxin oxide in its chemical character, for example, behaviour on oxidation and reduction, with sulphuric acid, and absence of hydroxyl, that no reasonable doubt can be entertained of the cyclic structure (IV) now assigned to it. It follows thence that the sulphoxide has the constitution indicated above (IV).

Further to confirm the phenothioxin structure for these substances, we have examined the naphthathioxin previously obtained by Mauthner (*Ber.*, 1906, **39**, 1345) from the interaction of β -naphthol sulphide and phosphoryl chloride. This substance may be converted into the oxide by interaction with hydrogen dioxide and into the dioxide with permanganate in glacial acetic acid. The behaviour of these substances agrees closely with that of the derivatives under consideration. Experiments have also been made to obtain the phenothioxins directly from the sulphides of *p*-cresol and of *p*-chlorophenol (compare Gazdar and Smiles, *loc. cit.*) by dehydrating agents. It is remarkable that negative results* were obtained even with hot sulphuric acid, zinc chloride at 200°, or boiling phosphoryl chloride. Since dichloro- and dimethylphenothioxin oxides are formed by the action of cold sulphuric acid on the sulphoxide, it appears that this reaction cannot be one of simple dehydration, for, if it were, it is to be expected that the sulphides would behave similarly, at any rate with hot dehydrating agents.

Such considerations lead to the assumption that the thionyl group plays some part in this reaction, and that the phenothioxin oxides are not the first products. This view is justified by the fact that the maximum yields of the cyclic compounds are only obtained by prolonging the reaction. In fact, if the action be stopped at an early period, by mixing the acid solution with water,

* It may be observed that the sulphide of β -naphthol yields the phenothioxin with the last-named of these reagents (Mauthner, *loc. cit.*), but the behaviour of this sulphide profoundly differs from that of other aromatic ortho-dihydroxysulphides in other respects, for example, oxidation.

entirely different products are obtained. It is thus evident that, although the phenothioxin oxides do not condense with phenolic ethers to give sulphonium salts, the cause of the inactivity of the parent sulphoxides must be sought in these initial products. The nature of the latter is now under investigation.

It may be observed that the phenothioxin oxides are not the only products of the prolonged action of sulphuric acid with the sulphoxides, for the yields are not good, and sulphonation is extensive.

The phenothioxin series is but little known; indeed, previous knowledge of this group is entirely due to Mauthner (*Ber.*, 1905, **38**, 1411; 1906, **39**, 1340), who synthesised two members of the series from *o*-thiolphenol and picryl chloride or 4-chloro-3:5-dinitrobenzoic acid. From the last-named substance, the parent compound was obtained by eliminating the nitro- and carboxyl groups.

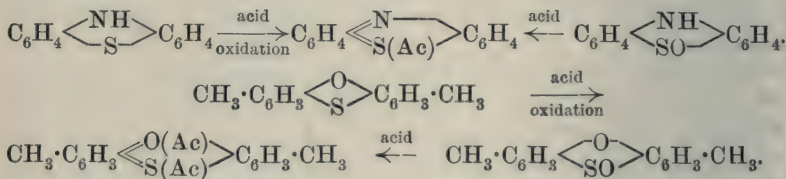
Observations made with the three series of derivatives embraced by the present experiments show that in certain respects these substances resemble the analogous series of thiodiphenylamine. It has been elsewhere shown that the *o*-sulphoxides of diphenylamine yield (Barnett and Smiles, *Trans.*, 1909, **95**, 1253) the intensely coloured azothionium salts with mineral acids, and a similar behaviour has now been observed with the *o*-sulphoxides of diphenyl ether, but in the latter case anhydrous acids of dehydrating power, for example, sulphuric acid, are necessary. Moreover, there is a striking similarity in the action of sulphuric acid on the sulphides of the two series. Thiodiphenylamine is at once oxidised by the cold reagent to the azothionium salt, sulphurous acid being liberated; the phenothioxins are also oxidised by this reagent, giving solutions of an intense blue colour. It may be further observed that these *o*-sulphoxides of diphenyl ether do not contain substituents of strongly acidic character, and they do not yield *S*-aryl derivatives when treated with a phenolic ether in sulphuric acid solution. The same fact has been observed with similar derivatives of diphenylamine *o*-sulphoxide, and it has been shown (Barnett and Smiles, *Trans.*, 1910, **97**, 369) that the disappearance of this characteristic reaction of the thionyl group is due to the immediate conversion of the sulphoxide to the azothionium salt. With sulphoxides of weaker basic power, the rearrangement to azothionium salt proceeds slowly, and the condensation may be effected before this has taken place.

To account for the absence of this characteristic reaction of the thionyl group from the phenothioxin oxides in this solvent, and to display the close analogy between this series and that of thiodiphenylamine, we consider it necessary to represent the products

of interaction of the phenothioxin oxides and sulphuric acid as phenothioxonium salts.

Attempts to isolate these substances have not as yet been successful, for on diluting the acid solution they are hydrolysed, and other substances are formed.

The relations between these series are indicated by the following formulæ:



EXPERIMENTAL.

2: 7-Dimethylphenothioxin, $\text{CH}_3 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C}_6\text{H}_3 \cdot \text{CH}_3$.

p-Cresol *o*-sulphoxide, in quantities of 20 grams at a time, was triturated with cold concentrated sulphuric acid, and the solution thus obtained was set aside at the atmospheric temperature for four hours. It was then carefully poured into cold water, and the muddy precipitate was collected and washed with water until free from sulphuric acid. The solid was triturated with aqueous alkali hydroxide, and a little alcohol was added to the mixture, which was then set aside for sixteen hours. The insoluble portion was then collected, washed until free from alkali, dried, and finally crystallised from dilute alcohol. The product melted indefinitely in the neighbourhood of 65°, and analysis showed that it was a mixture of the phenothioxin and its oxide. To obtain the substance in a pure condition, the product was converted into the oxide, and this was reduced.

Dimethylphenothioxin oxide was reduced in hot glacial acetic acid with zinc dust, and when reduction was complete, the excess of zinc dust was removed, and the filtrate mixed with water. An oil was precipitated, which quickly solidified; it was crystallised from dilute methyl alcohol, from which 2: 7-dimethylphenothioxin separated in colourless leaflets, melting at 74°:

0.1926 gave 0.3224 CO₂ and 0.0930 H₂O. C=73.9; H=5.3.

0.4110, in 16.79 c.c. of benzene gave Δ = -0.547°. M.W.=223.

C₁₄H₁₂OS requires C=73.7; H=5.2 per cent. M.W.=228.

Nitric acid readily attacks the substance, but no definite nitro-derivative could be isolated, for, on modifying the conditions, either the interaction was too violent or none took place.

The substance possesses an odour resembling that of geraniums; it is insoluble in water, and readily soluble in most organic media. It dissolves in concentrated sulphuric acid, the solution rapidly becoming blue, whilst sulphurous acid is evolved.

2: 7-Dimethylphenothioxin Oxide.

The crude product, obtained as described in a previous paragraph from *p*-cresol *o*-sulphoxide and sulphuric acid, was dissolved in cold glacial acetic acid. To this solution an amount of hydrogen dioxide was added slightly in excess of that required to convert all phenothioxin to its oxide. The mixture was set aside at the atmospheric temperature, and after twenty-four hours it was mixed with water. The solid product was recrystallised from dilute alcohol.

2: 7-Dimethylphenothioxin oxide forms colourless needles, which melt at 132–133°. It dissolves in sulphuric acid, the solution being of an intense blue colour:

0.1143 gave 0.2875 CO₂ and 0.0557 H₂O. C=68.7; H=5.4.

C₁₄H₁₂O₂S requires C=68.8; H=4.9 per cent.

2: 7-Dimethylphenothioxin Dioxide.

A solution of the oxide in cold acetic acid was mixed with the calculated quantity of finely powdered potassium permanganate. Solution of the permanganate was assisted by continual shaking, and finally the mixture was set aside for a few hours. Water was then added, and sulphurous acid was passed into the turbid mixture to effect complete decolorisation.

The solid was collected and crystallised from alcohol, when *2: 7-dimethylphenothioxin dioxide* was obtained in colourless prisms, which melted at 172°:

0.1132 gave 0.2693 CO₂ and 0.0485 H₂O. C=64.88; H=4.8.

C₁₄H₁₂O₃S requires C=64.62; H=4.6 per cent.

2: 7-Dichlorophenothioxin Oxide.

p-Chlorophenol *o*-sulphoxide was treated with sulphuric acid in the manner already described with the cresol derivative. Comparative experiments showed that the maximum yields of the phenothioxin derivative (about 25 per cent.) were obtained when the interaction was allowed to proceed for four hours. In this case, however, the product did not appear to contain the phenothioxin, for after it had been recrystallised from alcohol, *2: 7-dichlorophenothioxin oxide* was obtained in shining prisms, which melted at 168°:

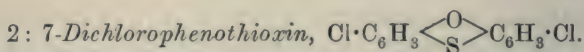
0.1005 gave 0.1880 CO_2 and 0.0200 H_2O . $\text{C}=51.0$; $\text{H}=2.2$.

0.1093 „ 0.2035 CO_2 „ 0.0255 H_2O . $\text{C}=50.7$; $\text{H}=2.5$.

$\text{C}_{12}\text{H}_6\text{O}_2\text{Cl}_2\text{S}$ requires $\text{C}=50.5$; $\text{H}=2.1$ per cent.

The substance gives an intense blue solution with cold sulphuric acid, but no sulphonium base is formed on adding a phenolic ether to this. In one experiment, excess of phenetole was added to the cold solution in sulphuric acid, and after about half an hour had elapsed, this was poured into water. The recrystallised product was found to contain dichlorophenothioxin, and a sample was isolated which melted at 134° . (Found, $\text{C}=53.2$; $\text{H}=2.7$. Calc., $\text{C}=53.5$; $\text{H}=2.2$ per cent.) No sulphonium base could be detected.

Attempts were made to obtain these phenothioxin derivatives by the action of other dehydrating agents with the hydroxy-sulphoxide or sulphide, but with negative results. The reagents employed were fused zinc chloride at 120° and 200° , boiling thionyl chloride, boiling phosphoryl chloride alone or in xylene solution, and boiling phosphorus trichloride. With the latter reagent, the sulphoxide was reduced to sulphide (m. p. 174°). (Found, $\text{C}=50.3$; $\text{H}=3.1$. Calc., $\text{C}=50.2$; $\text{H}=2.8$ per cent.) Warm sulphuric acid acting for one hour also gave negative results with *p*-cresol *o*-sulphide.



This substance was obtained by reducing the phenothioxin oxide with zinc dust in acetic acid, the process being similar to that already described with the dimethyl derivative. It separates from hot alcohol in long, slender needles, which melt at 135° :

0.1163 gave 0.2262 CO_2 and 0.0232 H_2O . $\text{C}=53.0$; $\text{H}=2.2$.

$\text{C}_{12}\text{H}_6\text{OCl}_2\text{S}$ requires $\text{C}=53.5$; $\text{H}=2.2$ per cent.

The substance is oxidised by concentrated sulphuric acid.

2: 7-Dichlorophenothioxin Dioxide.

This was prepared from the monoxide by oxidation, as described with the dimethyl derivative. It separates from hot alcohol in small, colourless prisms, which melt at 196° :

0.1310 gave 0.2322 CO_2 and 0.0294 H_2O . $\text{C}=48.3$; $\text{H}=2.49$.

$\text{C}_{12}\text{H}_6\text{O}_3\text{Cl}_2\text{S}$ requires $\text{C}=47.8$; $\text{H}=1.99$ per cent.

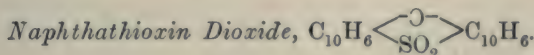


(a) *From Naphthathioxin and Hydrogen Dioxide.*—Naphthathioxin was prepared from β -dihydroxy- α -dinaphthyl sulphide by

interaction with phosphoryl chloride in boiling xylene, as described by Mauthner (*Ber.*, 1906, **39**, 1346). A solution of this substance in a mixture of acetic acid and anhydride, which contained a slight excess of hydrogen dioxide, was set aside at the atmospheric temperature. After four days the mixture was poured into water, and the solid product which then separated was collected and recrystallised from hot acetic acid. Naphthathioxin oxide, prepared in this manner, forms pale yellow needles, which darken and melt at 221°. (Found, C=75·3; H=4·0. Calc., C=75·9; H=3·8 per cent.)

The solutions in sulphuric acid are of a deep blue colour. This substance has been previously prepared by Mauthner (*loc. cit.*) by the oxidation of naphthathioxin with chromic acid. The product of this method was red, but it melted at the same temperature as that now given.

(b) *From β-Dihydroxy-α-dinaphthyl Sulphide and Sulphuric Acid.*—This substance readily dissolves in sulphuric acid, but oxidation sets in immediately, the solution becoming blue, and sulphurous acid being evolved. In one experiment, the mixture was set aside for twenty-four hours, and then dealt with as described in the preparation of the phenothioxin oxides from the sulphoxides of *p*-cresol and *p*-chlorophenol. The product was repeatedly crystallised from hot acetic acid, and finally naphthathioxin oxide was obtained. It was identified by the melting point of a mixture with that substance obtained from other sources.



Naphthathioxin was oxidised in acetic acid solution with potassium permanganate in the usual manner. The product was crystallised from boiling acetic acid, in which it is sparingly soluble. It forms colourless prisms, which melt at 268°:

0·1043 gave 0·2744 CO₂ and 0·0361 H₂O. C=71·74; H=3·8.

C₂₀H₁₂O₃S requires C=72·3; H=3·6 per cent.

The Ethers of p-Cresol and p-Chlorophenol o-Sulphoxides.

The methyl ether of *p*-cresol *o*-sulphoxide was prepared from the corresponding phenol by interaction with methyl iodide in alkaline solution of methyl alcohol. The product of the reaction was treated in a manner similar to that described in the alkylation of phenol *p*-sulphoxide (*Trans.*, 1907, **91**, 1120). It was purified by crystallisation from ethyl acetate, when it was obtained in colourless prisms, which melted at 134°. A mixture of this substance and the product obtained by direct sulphination of *p*-tolyl methyl

ether melted at the same temperature. The constitution of the latter has been previously discussed (Le Rossignol and Smiles, *Trans.*, 1908, **93**, 745).

The ethyl ether of *p*-chlorophenol *o*-sulphoxide was prepared by direct sulphonation of *p*-chlorophenetole, the process being similar to that formerly described (Le Rossignol and Smiles, *loc. cit.*) with *p*-tolyl methyl ether.

The substance crystallises from ethyl acetate in fine needles, which melt at 145°:

0.1130 gave 0.2234 CO₂ and 0.0485 H₂O. C=53.9; H=4.7.

C₁₆H₁₆O₃Cl₂S requires C=53.48; H=4.46 per cent.

Both of these ethers of *p*-cresol and *p*-chlorophenol sulphoxide give blue solutions with sulphuric acid, and condense in that medium with phenetole, when the colour is discharged. The corresponding hydroxy-sulphoxides* do not undergo this condensation under like conditions.

In conclusion, we desire to thank the Research Fund Committee of the Society for a grant which has defrayed the cost of these experiments.

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LII.— α -*p*-Hydroxy-m-methoxyphenylethylamine and the Resolution of α -*p*-Hydroxyphenylethylamine.

By CHARLES WATSON MOORE.

It has several times recently been shown that the enantiomorphously related compounds may differ considerably in their physiological action. Thus, Cushny (*J. Physiol.*, 1904, **30**, 176) has shown that *l*-hyoscyamine is considerably more active physiologically than the corresponding *d*-base (compare also *Trans.*, 1909, **95**, 1969). Similarly, the same author has noted (*Pharm. Journ.*, 1909, **82**, 56) that the stereoisomeric epinephrines ("adrenalines") (β -3:4-trihydroxy- β -phenylethylmethyamines) show great differences in the relative intensities of their effect on the blood pressure.

The base α -*p*-hydroxyphenylethylamine, described by Tutin, Caton, and Hann (*Trans.*, 1909, **95**, 2113), exerts an action on the

* It was formerly stated in error (Gazdar and Smiles, *Trans.*, 1910, **93**, 2251) that the sulphoxide of *p*-chlorophenol undergoes this condensation.

blood pressure somewhat similar to that of epinephrine, although in a less degree, and, since the former base contains an asymmetric carbon atom, it was considered of interest to ascertain whether the optically active bases, obtained by its resolution, would differ in physiological activity. α -*p*-Hydroxyphenylethylamine *d*-camphorsulphonate was therefore prepared and submitted to fractional crystallisation, when the salt of the lævorotatory base was easily obtained in a pure condition.

l- α -*p*-Hydroxyphenylethylamine *d*-camphorsulphonate melts at 203—205°, and the specific rotation of the base contained in it, calculated from that of the salt, is $[\alpha]_D -7.9^\circ$. The salt of the *d*-base could not be obtained in a pure condition, the specific rotation of the base contained in it being $[\alpha]_D +6.9^\circ$. Optically pure benzoyl derivatives were, however, obtained from both of the stereoisomeric bases. The effect on the blood pressure of the *l*- and *dl*-bases was determined by Dr. H. H. Dale, of the Wellcome Physiological Research Laboratories, to whom the author now expresses his thanks. No difference in physiological activity between the two bases was observed, and it is therefore evident that in this case the enantiomorphous forms possess an equal degree of physiological activity.

A quantity of acetovanillone (4-hydroxy-3-methoxyacetophenone) being available, it was considered of interest to prepare the corresponding α -*p*-hydroxy-*m*-methoxyphenylethylamine from it. This compound was obtained by the reduction of acetovanilloneoxime, and its hydrochloride and benzoyl derivatives have also been characterised. It has been found by Dr. H. H. Dale, as was anticipated, that the hydroxymethoxy-base is slightly less active physiologically than the above-mentioned α -*p*-hydroxyphenylethylamine.

EXPERIMENTAL.

α -p-Hydroxy-m-methoxyphenylethylamine.

Acetovanillone (4-hydroxy-3-methoxyacetophenone), as obtained from the rhizome of *Apocynum androsaemifolium*, Linné (Moore, Trans., 1909, 95, 734), was converted into its oxime in the usual manner.

Eighteen grams of acetovanilloneoxime were dissolved in 250 c.c. of aqueous methyl alcohol, and twice the theoretical amount of 3 per cent. sodium amalgam gradually introduced, the mixture being kept acid by the frequent addition of acetic acid. When all reaction had ceased, water was added, the alcohol distilled off, and the aqueous liquid extracted with ether to remove unchanged oxime, after which it was rendered alkaline by means of sodium carbonate, and thoroughly extracted with amyl alcohol. The amyl-

alcoholic liquids were extracted with successive quantities of dilute hydrochloric acid, and the combined acid liquids concentrated under diminished pressure, when, on cooling, *α -p-hydroxy-m-methoxyphenylethylamine hydrochloride* separated in glistening prisms. This salt is readily soluble in water and alcohol, but can be recrystallised from a mixture of alcohol and ethyl acetate. The quantity so obtained amounted to about 8.5 grams:

0.1490 gave 0.2938 CO_2 and 0.0936 H_2O . $\text{C}=53.7$; $\text{H}=7.0$.

0.1710 „ 0.1180 AgCl . $\text{Cl}=17.0$.

$\text{C}_9\text{H}_{13}\text{O}_2\text{N}\cdot\text{HCl}$ requires $\text{C}=53.1$; $\text{H}=6.9$; $\text{Cl}=17.4$ per cent.

A methoxyl determination by Perkin's modification of the Zeisel method gave the following result:

0.2136 gave 0.2445 AgI . $\text{OMe}=15.1$.

$\text{C}_8\text{H}_{11}\text{ONCl}\cdot\text{OMe}$ requires $\text{OMe}=15.2$ per cent.

α -p-Hydroxy-m-methoxyphenylethylamine was obtained from its hydrochloride by the action of sodium ethoxide on an alcoholic solution of the salt. Five grams of the hydrochloride were dissolved in about 25 c.c. of warm absolute alcohol, and to the solution 0.53 gram of sodium, dissolved in 10 c.c. of absolute alcohol, was added. The precipitated sodium chloride was removed by filtration, and the filtrate cooled, when the *base* separated in glistening prisms, melting at 158° . The quantity so obtained was only 1.5 grams, and on concentrating the alcoholic mother liquor, only amorphous products were obtained. As only 95 per cent. of the theoretical amount of sodium ethoxide was employed for the liberation of the base, this change can only be attributed to the unstable nature of the substance in solution. A similar phenomenon was observed on recrystallising the base, but the latter, when in the crystalline state, is quite stable:

0.1338 gave 0.3180 CO_2 and 0.0970 H_2O . $\text{C}=64.8$; $\text{H}=8.0$.

0.2806 „ 20.6 c.c. N_2 at 23° and 755 mm. $\text{N}=8.2$.

$\text{C}_9\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C}=64.7$; $\text{H}=7.8$; $\text{N}=8.4$ per cent.

A methoxyl determination by Perkin's modification of the Zeisel method gave the following result:

0.2240 gave 0.3095 AgI . $\text{OMe}=18.2$.

$\text{C}_8\text{H}_{10}\text{ON}\cdot\text{OMe}$ requires $\text{OMe}=18.5$ per cent.

The *dibenzoyl* derivative, prepared by the Schotten-Baumann method, crystallises from alcohol in glistening plates, melting at 178° :

0.1326 gave 0.3574 CO_2 and 0.0686 H_2O . $\text{C}=73.5$; $\text{H}=5.7$.

$\text{C}_{23}\text{H}_{21}\text{O}_4\text{N}$ requires $\text{C}=73.6$; $\text{H}=5.6$ per cent.

α -p-Hydroxy-m-methoxy-N-benzoylphenylethylamine was obtained by heating the dibenzoyl derivative for some hours with a 10 per

cent. alcoholic solution of potassium hydroxide. It crystallises from alcohol in glistening needles, melting at 168° :

0.1230 gave 0.3170 CO_2 and 0.0711 H_2O . $\text{C} = 70.3$; $\text{H} = 6.4$.

$\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C} = 70.1$; $\text{H} = 6.3$ per cent.

The Resolution of α -p-Hydroxyphenylethylamine.

α -p-Hydroxyphenylethylamine hydrochloride was first prepared by Tutin, Caton, and Hann (*loc. cit.*), by the reduction of *p*-hydroxyacetophenoneoxime, according to the above-described method for the preparation of α -p-hydroxy-*m*-methoxyphenylethylamine hydrochloride. The yield of hydrochloride obtained by these authors was only about 30 per cent. of the theoretical. In view of the above-recorded observation respecting the instability of α -p-hydroxy-*m*-methoxyphenylethylamine, it seemed advisable to isolate α -p-hydroxyphenylethylamine hydrochloride without ever liberating the free base. The following modification of the original method was accordingly employed.

Twenty-seven grams of *p*-hydroxyacetophenoneoxime were dissolved in 300 c.c. of aqueous methyl alcohol, and twice the theoretical amount of 3 per cent. sodium amalgam gradually introduced, the mixture being kept acid by the frequent addition of acetic acid. When the reduction was finished, hydrochloric acid, in slight excess, was added, and the solution evaporated to complete dryness under diminished pressure. During the concentration most of the sodium chloride separated, and was removed by filtration. The final residue consisted of the hydrochloride of the base, together with a little sodium chloride, from which the former was obtained by extraction with cold absolute alcohol. The yield was about 70 per cent. of the theoretical.

α -p-Hydroxyphenylethylamine *d*-camphorsulphonate was obtained by the interaction of α -p-hydroxyphenylethylamine hydrochloride and silver *d*-camphorsulphonate in aqueous solution. The precipitated silver chloride was removed by filtration, and the filtrate evaporated to dryness under diminished pressure.

1- α -p-Hydroxyphenylethylamine *d*-Camphorsulphonate.—The crystalline camphorsulphonate thus obtained was dissolved in hot absolute alcohol, when, on keeping for a short time, a crop of crystals was obtained, melting at 200 — 202° . On recrystallisation from alcohol, the melting point rose to 203 — 205° , when it remained constant. The salt forms small, glistening plates, readily soluble in water and hot alcohol:

0.3154 gave 0.2010 BaSO_4 . $\text{S} = 8.7$.

$\text{C}_{18}\text{H}_{27}\text{O}_5\text{NS}$ requires $\text{S} = 8.7$ per cent.

0.4838, made up to 20 c.c. with water, gave, in a 2-dcm. tube, $\alpha_D + 0^\circ 32'$, whence $[\alpha]_D + 11.0^\circ$; $[M]_D + 40.6^\circ$.

0.4480, made up to 20 c.c. with water, gave, in a 2-dcm. tube, $\alpha_D + 0^\circ 29'$, whence $[\alpha]_D + 10.8^\circ$; $[M]_D + 39.8^\circ$.

The molecular rotation of *d*-camphorsulphonic acid is $[M]_D + 51^\circ$, whence the basic ion has $[\alpha]_D - 7.9^\circ$.

The 1-*dibenzoyl* derivative, prepared by the Schotten-Baumann method, crystallises from alcohol in long needles, melting at 210° :

0.1452 gave 0.4090 CO_2 and 0.0745 H_2O . $\text{C} = 76.8$; $\text{H} = 5.7$.

$\text{C}_{22}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{C} = 76.5$; $\text{H} = 5.5$ per cent.

A determination of its specific rotatory power gave the following result:

0.3502, made up to 20 c.c. with chloroform, gave $\alpha_D - 0^\circ 40'$ in a 2-dcm. tube, whence $[\alpha]_D - 19.0^\circ$.

1- α -*Hydroxy-N-benzoylphenylethylamine* was formed on heating the dibenzoyl derivative with a 10 per cent. alcoholic solution of potassium hydroxide. It crystallised from dilute methyl alcohol in small, glistening needles, containing 1.5 molecules of water of crystallisation. The anhydrous substance melts at 144° . This substance appears to be dimorphous, as the racemic modification, prepared by Tutin, Caton, and Hann (*loc. cit.*), forms large, hexagonal prisms, melting at 156° :

0.5040 (air dried) gave, on heating at 110° , 0.0495 H_2O . $\text{H}_2\text{O} = 9.8$.

0.1388 * gave 0.3804 CO_2 and 0.0794 H_2O . $\text{C} = 74.7$; $\text{H} = 6.3$.

$\text{C}_{15}\text{H}_{15}\text{O}_2\text{N} \cdot 1.5\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 10.0$ per cent.

$\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C} = 74.8$; $\text{H} = 6.2$ per cent.

A determination of its specific rotatory power gave the following result:

0.2150,* made up to 20 c.c. with chloroform, gave $\alpha_D - 1^\circ 8'$ in a 2-dcm. tube, whence $[\alpha]_D - 52.7^\circ$.

The alcoholic mother liquor from which the first crop of crystals had been removed, as above described, was concentrated to a small volume, when a quantity of crystals, melting from 180° to 190° , was obtained. This was removed, and the mother liquor mixed with a large volume of ethyl acetate, when it yielded a final fraction, melting at 163 — 165° . This final fraction consisted largely of the salt of the dextrorotatory modification, but all attempts to obtain it pure were unsuccessful.

A determination of its specific rotatory power gave the following result:

* Anhydrous substance.

0.4338, made up to 20 c.c. with water, gave $\alpha_D + 0^\circ 42.7'$ in a 2-dcm. tube, whence $[\alpha]_D + 16.4^\circ$; $[M]_D + 60.5^\circ$.

The molecular rotation of *d*-camphorsulphonic acid is $[M]_D + 51^\circ$, whence the basic ion has $[\alpha]_D + 6.9^\circ$.

The *d*-dibenzoyl derivative, prepared by the Schotten-Baumann method, crystallised from alcohol in long needles, melting at 205° . After recrystallising from ethyl acetate, the melting point was constant at 210° :

0.1460 gave 0.4104 CO_2 and 0.0745 H_2O . $\text{C} = 76.6$; $\text{H} = 5.6$.

$\text{C}_{22}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{C} = 76.5$; $\text{H} = 5.5$ per cent.

A determination of its specific rotatory power gave the following result:

0.3348, made up to 20 c.c. with chloroform, gave $\alpha_D + 0^\circ 37'$ in a 2-dcm. tube, whence $[\alpha]_D + 18.4^\circ$.

d-*a*-p-Hydroxy-N-benzoylphenylethylamine was formed on heating the dibenzoyl derivative with a 10 per cent. solution of alcoholic potassium hydroxide. It crystallises from dilute methyl alcohol in glistening needles, containing 1.5 molecules of water of crystallisation. The anhydrous substance melts at 144° :

0.2850 (air dried), on heating at 110° , lost 0.0275 H_2O . $\text{H}_2\text{O} = 9.6$.

0.1410 * gave 0.3880 CO_2 and 0.0796 H_2O . $\text{C} = 75.0$; $\text{H} = 6.2$.

$\text{C}_{15}\text{H}_{15}\text{O}_2\text{N} \cdot 1.5\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 10.0$ per cent.

$\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C} = 74.8$; $\text{H} = 6.2$ per cent.

A determination of its specific rotatory power gave the following result:

0.1494,* made up to 20 c.c. with chloroform, gave $\alpha_D + 0^\circ 49'$ in a 2-dcm. tube, whence $[\alpha]_D + 54.6^\circ$.

In conclusion, the author wishes to express his thanks to Mr. Frank Tutin for suggesting this investigation.

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LONDON, E.C.

* Anhydrous substance.

LIII.—*The Formation and Reactions of Imino-compounds. Part XV. The Production of Imino-derivatives of Piperidine Leading to the Formation of the $\beta\beta$ -Disubstituted Glutaric Acids.*

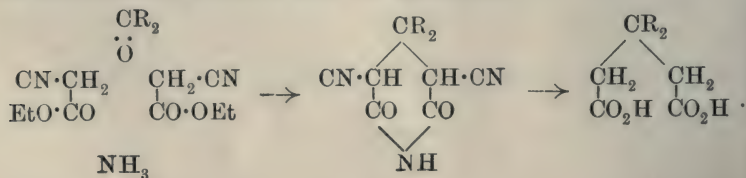
By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

THE methods at present in use for the production of the $\beta\beta$ -disubstituted glutaric acids are, for the most part, long and tedious operations, requiring the aid of large quantities of expensive material. Thus, $\beta\beta$ -dimethylglutaric acid,



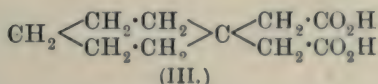
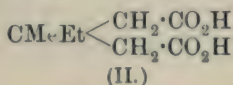
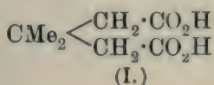
which is the simplest and best known member of this series, can be prepared either by the oxidation of dimethyldihydroresorcinol (Crossley, *Trans.*, 1899, **75**, 777; Komppa, *Ber.*, 1899, **32**, 1423), or by the condensation of ethyl sodiocyanoacetate with ethyl $\beta\beta$ -dimethylacrylate, and the subsequent hydrolysis of the condensation product (Perkin and Thorpe, *Trans.*, 1899, **75**, 49). Both these methods of formation yield the acid in large quantities, but the preparation of the initial material always occupies a considerable period of time; moreover, the above-mentioned reactions have only been applied to the formation of $\beta\beta$ -dimethylglutaric acid; their application to the formation of higher members of the series would be prohibitive from the point of view of expense of material. Unfortunately, the reactions by which the β -monosubstituted glutaric acids can be prepared, that is, by the condensation of aldehydes with ethyl malonate or ethyl cyanoacetate in the presence of piperidine (Komnenos, *Annalen*, 1883, **218**, 145; Knoevenagel, *Ber.*, 1898, **31**, 2588), do not yield satisfactory results when the aldehydes are replaced by ketones, and only small yields of the condensation products are obtained by these processes.

This difficulty has been partly overcome by the process introduced by Guareschi (*Atti R. Accad. Sci. Torino*, 1900–1901, **36**, 443), who condensed ethyl cyanoacetate with ketones in the presence of ammonia, and obtained a piperidine derivative, which yields the $\beta\beta$ -disubstituted glutaric acid on hydrolysis:



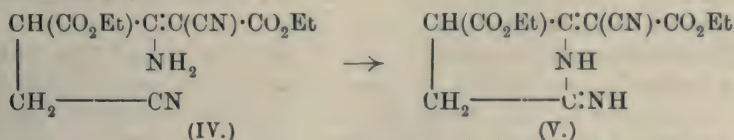
By the aid of this reaction, Guareschi was able to prepare a number of $\beta\beta$ -disubstituted glutaric acids by varying the nature of the ketone used in the initial condensation.

Although this reaction yields the substituted glutaric acid in a very pure form, we have found it to be a matter of some difficulty to establish the right conditions for the formation of the piperidine derivative in any quantity, and as we wished to prepare a large amount of $\beta\beta$ -dimethylglutaric acid for the purposes of another research, we decided to search for some method which would yield the acid both rapidly and cheaply. Ultimately we were successful in finding a process, not only leading to the formation of this acid, but one which could be used for the formation of a large number of homologues of glutaric acid substituted in the β -position. As it was thought advisable to establish the general character of this method, three typical examples were selected, namely, $\beta\beta$ -dimethylglutaric acid (I), β -methyl- β -ethylglutaric acid (II), and *cyclohexane*-1:1-diacetic acid (III):



and the successive stages of the reaction were carefully followed in each case.

The principle on which the new method is based is as follows. In a previous communication it was shown that an open-chain compound, consisting of four carbon atoms and one nitrogen atom, readily passes into an imino-ring when there is a nitrile group and an amino-group at the opposite ends of the chain. Thus the open-chain compound (IV) was found to pass readily into the pyrrole derivative (V):



The ease with which the piperidine ring is usually formed suggested that in all probability a six-membered open chain of the type (VI) would also pass into the six-membered ring (VII), thus:



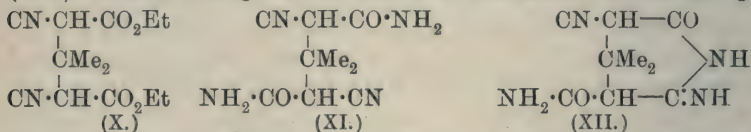
or, in other words, a nitrile-amide of formula (VIII) would pass into an imino-piperidone of formula (IX):



It was, moreover, noticed that imino-compounds of this type are characterised by being practically insoluble in water as well as in most of the usual organic solvents, and it therefore seemed likely that if such a compound could be formed in some simple condensation, it would be at once precipitated from the solution, and hence give rise to a practically quantitative yield of the condensation product, however small the original tendency for its formation might be.

The substance which at once suggested itself as a means of ascertaining this point was cyanoacetamide, $\text{CN} \cdot \text{CH}_2^* \cdot \text{CO} \cdot \text{NH}_2$, a compound which has been shown by Henry (*Jahresber.*, 1889, 638) and by Errera (*Gazzetta*, 1896, **26**, 208) to possess properties very similar to those of ethyl cyanoacetate, and to have a hydrogen atom, marked above with an asterisk, which is replaceable by sodium.

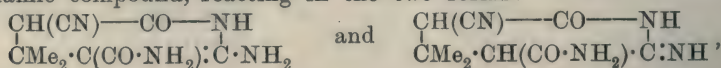
As already mentioned, ethyl cyanoacetate condenses with acetone in the presence of piperidine to give a small yield of the condensation product (X). If therefore cyanoacetamide were substituted for ethyl cyanoacetate, it might be expected that the initial product (XI) would at once pass into the imino-compound (XII), which, owing to its insoluble character, would be pre-



cipitated from the solution, giving rise to a fresh production of condensation product, and this in its turn would be precipitated, and so on until the reaction was complete.

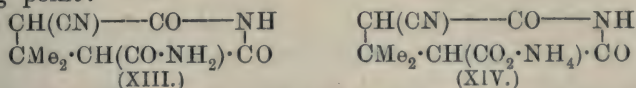
This assumption proved to be correct, for it was found that when two molecular proportions of cyanoacetamide and one of acetone were dissolved in cold water and treated with a small quantity of piperidine or aqueous sodium hydroxide, the resulting yellow solution slowly deposited a crystalline precipitate, which, when complete, weighed more than the amount of cyanoacetamide used in the experiment.

Investigation showed this substance to be a tautomeric ketimino-enamic compound, reacting in the two forms:



but having a very short imino-phase,* a conclusion which was arrived at as the result of the following experiments:

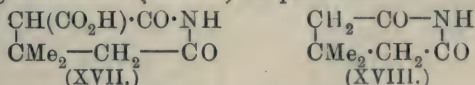
(1) The substance is a mono-acid base, and yields a well-defined platinichloride. It forms a clear solution with dilute hydrochloric acid, which, if immediately treated with sodium acetate, deposits the imino-compound practically unchanged, but, if allowed to remain, slowly deposits the imide (XIII), formed by the hydrolysis of the imino-form of the tautomeric compound. The transformation of the imino-compound (XII) into the imide (XIII) is complete if the solution of the base in dilute hydrochloric acid is raised to the boiling point:



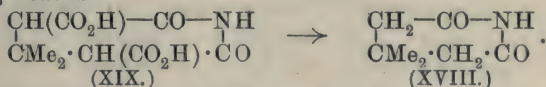
(2) When the base (XII) is boiled for a long time with water, ammonia is eliminated, and if the operation is continued until all ammonia has been evolved, the product is found to be the cyano-acid (XV). It is evident that the ammonium salt of this acid (XIV) is first formed, but that on boiling with water it dissociates, yielding the free acid:



(3) When the above cyano-acid (XV) is heated, carbon dioxide is eliminated, and the nitrile (XVI) is formed. This substance is also produced when a solution of the base (XII) in dilute hydrochloric acid is boiled for some hours. When the cyano-acid is boiled with alkali, the alkali salt of the carboxylic acid (XVII) is formed, and when the free acid is heated, carbon dioxide is evolved, and $\beta\beta$ -dimethylglutarimide (XVIII) is produced:



(4) When the base (XII) is treated with excess of sodium hydroxide, it forms a clear yellow solution, the colour of which disappears on boiling, ammonia being subsequently evolved on further heating. The ultimate product, after all ammonia has been eliminated, is the alkali salt of the dibasic acid (XIX), the free acid from which passes into $\beta\beta$ -dimethylglutarimide (XVIII) on being heated:



* As the compound gives no colour with ferric chloride there is probably no enolic phase.

The yield of $\beta\beta$ -dimethylglutarimide by this last process is not very good, as the action of alkali on the base also proceeds in another direction, with the formation of some acetone and malonic acid. The cause of this rather remarkable decomposition is still under investigation.

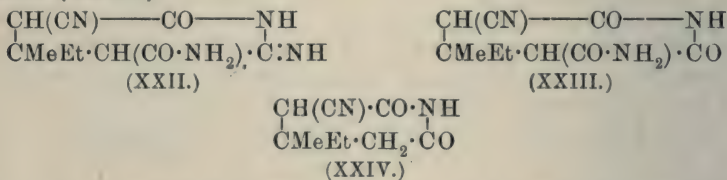
(5) When the base (XII) is heated with 70 per cent. sulphuric acid for three hours, it is quantitatively converted into $\beta\beta$ -dimethylglutaric acid (XXI):



The constitution of the condensation product of cyanoacetamide and acetone is there clearly established. In order, however, to show that the method is of general application, we decided, as already mentioned, to investigate two other cases, and selected methyl ethyl ketone and *cyclohexanone* for experiment.

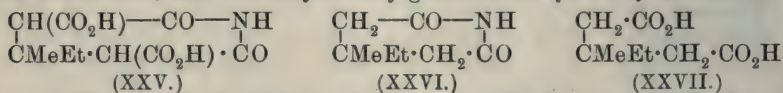
Both these ketones readily condense with cyanoacetamide in the presence of piperidine or sodium hydroxide, and in each case a satisfactory yield of the condensation product is obtained.

Methyl ethyl ketone yields the imino-compound (XXII), which, on warming with dilute hydrochloric acid, is converted into the imide (XXIII):



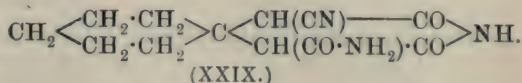
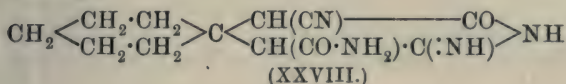
from which the nitrile (XXIV) is produced by the prolonged action of boiling dilute hydrochloric acid.

Alkalis hydrolyse the imino-compound to the dibasic acid (XXV), but here again a certain amount of methyl ethyl ketone is regenerated during the hydrolysis, and the yield of the dibasic acid is, consequently, not good. When the acid is heated, carbon dioxide is eliminated, and β -methyl- β -ethylglutarimide (XXVI) is formed:

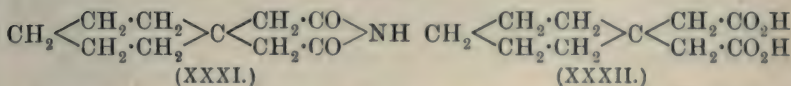
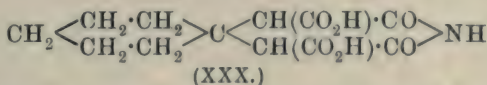


When the imino-compound (XXII) is boiled with 70 per cent. sulphuric acid, it is completely transformed into β -methyl- β -ethylglutaric acid (XXVII). This acid has been prepared by Guareschi (*loc. cit.*), but was not characterised by the formation of derivatives. We have therefore prepared the anhydride and the naphthylamic acid.

The imino-compound (XXVIII), which is formed from *cyclohexanone* and cyanoacetamide, undergoes a similar series of changes. Thus, with warm dilute hydrochloric acid, it yields the imide (XXIX):



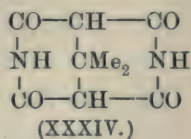
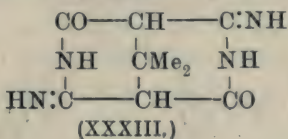
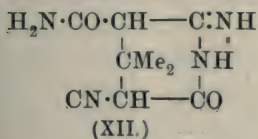
When boiled with aqueous potassium hydroxide until free from ammonia, some *cyclohexanone* is eliminated, but it is, for the most part, converted into the dibasic acid (XXX), which, on being heated, is converted into the imide of *cyclohexane-1:1*-diacetic acid (XXXI). With sulphuric acid, the imino-compound (XXVIII) is completely converted into *cyclohexane-1:1*-diacetic acid (XXXII):



cycloHexane-1:1-diacetic acid is a well-defined crystalline substance, which melts at 181° , and gives an anhydride melting at 73° . It was characterised by the formation of derivatives.

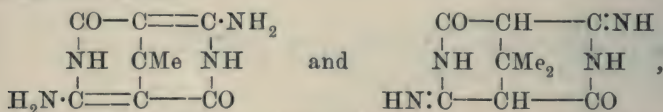
These examples therefore show clearly that the method, so far as the simpler ketones are concerned, is of general application, and that by its means the $\beta\beta$ -disubstituted glutaric acids can be readily prepared in quantity.

During the experiments with these imino-compounds derived from ketones and cyanoacetamide, it was noticed that under certain conditions they readily undergo a further imino-condensation with the formation of a second six-membered ring having three carbon atoms in common with the first. Thus, when the imino-compound derived from acetone and cyanoacetamide (XII) is treated with sodium ethoxide in alcohol, a sparingly soluble sodium salt is formed, which, when treated in aqueous solution with acetic acid, yields a crystalline substance the reactions of which show it to be the di-iminodi-imide represented by formula (XXXIII):



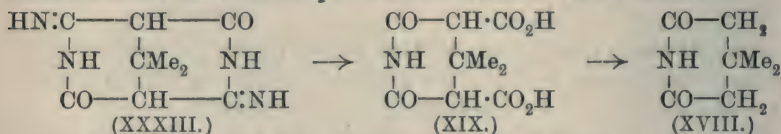
The constitution of this substance follows from the following experimental data:

(1) It is a di-acid, tautomeric di-imino-diamino-compound, reacting in the two forms:



but has only a short imino-phase. This is shown by its behaviour towards dilute hydrochloric acid, in which it forms a clear solution when cold, but from which the original substance is precipitated practically unchanged on the addition of sodium acetate. When the solution in dilute hydrochloric acid is warmed, both imino-groups are at once eliminated, and the di-imide (XXXIV) is precipitated from the hot solution.

(2) When boiled with aqueous potassium hydroxide, one imido-ring is broken, and if the action of the alkali is continued until all ammonia has been evolved, the dibasic acid (XIX) can be obtained from the product. The constitution of this dibasic acid was proved, as in the former case, by the production of $\beta\beta$ -dimethylglutarimide from it on heating, and therefore the decomposition of the di-imino-di-imide must have taken place in accordance with the scheme:

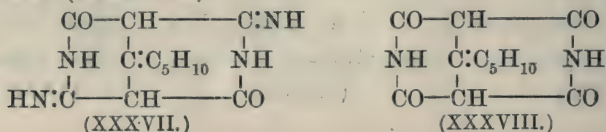


(3) When boiled with 70 per cent. sulphuric acid, the di-imino-di-imide is completely converted into $\beta\beta$ -dimethylglutaric acid.

The formation of the double ring is also shown by the imino-compounds from methyl ethyl ketone and *cyclohexanone* (XXII and XXVIII). Thus, the first-named yields the di-imino-di-imide (XXXV), which, on warming with dilute hydrochloric acid, passes into the di-imide (XXXVI):



whilst the imino-compound from *cyclohexanone* yields the di-imino-di-imide (XXXVII), which is converted by hydrochloric acid into the di-imide (XXXVIII):

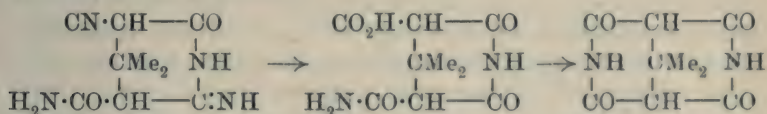


These substances behave in the same manner as the di-imino-di-imide from acetone, and are completely hydrolysed by sulphuric acid to the corresponding $\beta\beta$ -disubstituted glutaric acids.

The formation of the double ring in this manner is certainly remarkable, but the fact that it is so readily broken by alkali hydroxide, when, as is well known, the imides of the glutaric series are very stable towards this reagent, shows that it is under greater strain than the single ring.

The double ring is, however, produced by other reagents than sodium ethoxide; thus it is the first product formed by the action of aqueous alkali hydroxides on the imino-imides. This fact can be demonstrated in the following way. When the imino-imide is dissolved in dilute aqueous alkali, a yellow solution is formed, the colour of which is rapidly discharged on warming. If the solution is cooled as soon as the colour has disappeared and is then acidified with acetic acid, the di-imino-di-imide is precipitated in the pure condition.

The double-ring compounds are also formed under conditions which usually yield the single-ring imides from the corresponding γ -nitrile carboxylic acids. Thus, when the imino-imides are boiled with dilute sulphuric acid, the clear solution, on being boiled, slowly deposits the crystalline dicyclic di-imide. This reaction is probably represented by the scheme:



and does not involve the previous formation of the di-imino-di-imido-compound.

EXPERIMENTAL.

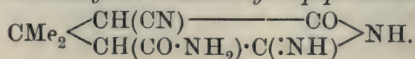
Cyanoacetamide, $\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$.

This substance was originally prepared by Hoff (*Jahresber.*, 1874, 561), and more recently by Henry (*Bull. Soc. chim.*, 1887, [ii], 48, 656) and Hesse (*Amer. Chem. J.*, 1896, 18, 724). We find that it may be quickly prepared by the following simplified process.

One hundred grams of ethyl cyanoacetate are mixed in a wide-mouthed stoppered bottle with 75 c.c. of strong ammonia, and shaken vigorously. After three minutes the solution becomes homogeneous and warm, when it is cooled under running water and shaken for twenty minutes. The crystals are then collected, washed with a little cold alcohol, and recrystallised from a small amount of hot alcohol. The yield obtained in this way is 85 per cent. of the theoretical, and a further quantity, representing 10 per cent., can be recovered from the mother liquors on evaporating them under

diminished pressure. Pure cyanoacetamide forms colourless needles, which melt at 118.5° .

Condensation of Acetone with Cyanoacetamide: 6-Imino-3-cyano-5-carbamyl-4:4-dimethyl-2-piperidone,



This condensation is effected in aqueous solution in the presence of a small quantity of piperidine or alkali hydroxide; the conditions found to give the best yield were as follows.

One hundred grams of cyanoacetamide were dissolved in a sufficient quantity of cold water, and the clear solution was mixed with 45 grams of acetone.* The solution was then warmed to 20° , and 1 c.c. of piperidine or 1 c.c. of a 30 per cent. solution of potassium hydroxide in water added, the solution being kept for twenty-four hours. At the end of this time the large quantity of crystalline material which had separated was filtered from the yellow solution, washed with water, and dried on a porous plate. It weighed 105 grams (theory, 123 grams), and was found to be completely soluble in cold dilute hydrochloric acid. The mother liquor from the crystals deposited, after some time, a further small quantity of crystalline material, only part of which dissolved in dilute hydrochloric acid. The two substances present in this mixture were separated by grinding with cold dilute hydrochloric acid, filtering, and precipitating the soluble portion from the filtrate by the addition of sodium acetate solution. In this way a further 10 grams of basic substance were obtained identical with that derived from the first precipitation, giving therefore a total yield of 93 per cent. The piperidone derivative obtained in this manner crystallises from water in small, colourless prisms, which melt to a yellow liquid, and then decompose at 234° . The base is only very sparingly soluble in the usual organic solvents, and since recrystallisation from water gives rise to a certain amount of decomposition, it is best purified by dissolving in cold dilute hydrochloric acid and reprecipitating by the addition of sodium acetate:

0.1895 gave 0.3588 CO_2 and 0.1006 H_2O . $\text{C}=51.64$; $\text{H}=5.9$.

0.1551 „ 37.0 c.c. N_2 at 19° and 733 mm. $\text{N}=26.95$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{N}_4$ requires $\text{C}=51.9$; $\text{H}=5.8$; $\text{N}=26.9$ per cent.

The piperidone derivative reacts as a monacid base, and forms stable salts with mineral acids.

The *platinichloride* separates as a yellow, sandy powder when a solution of platinic chloride is added to a concentrated solution of

* In the earlier experiments acetone from the bisulphite compound was used. It was found later that commercially pure acetone gave equally good results.

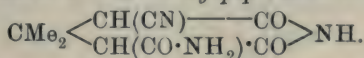
the base in excess of hydrochloric acid. Care must be taken, however, to keep the temperature as low as possible, and to facilitate the separation of the salt by scratching; otherwise some ammonium platinichloride will also separate, owing to the hydrolysis of the imino-group by the hydrochloric acid present:

0.3300 gave 0.0770 Pt. $Pt = 23.33$.

$(C_9H_{12}O_2N_4)_2 \cdot H_2PtCl_6$ requires $Pt = 23.5$ per cent.

When the piperidone base is boiled for a long time with water, ammonia is evolved together with some acetone; the compounds formed are described on p. 432. It dissolves in aqueous sodium hydroxide, forming a yellow solution, from which the colour is discharged on warming; the cause of this change is explained on p. 436. The prolonged action of boiling alkali yields $\beta\beta$ -dimethylglutarimide as chief product, whereas the ultimate hydrolysis by concentrated mineral acids gives a quantitative yield of $\beta\beta$ -dimethylglutaric acid. During the preparation of the above piperidone base either by the aid of piperidine or of alkali hydroxide, a small quantity of a second substance is always produced. In the piperidine experiment, this substance separates from the mother liquor on keeping after the imino-compound has been collected, and can be readily isolated from the chief product of the reaction, owing to its insolubility in dilute hydrochloric acid. In the potassium hydroxide experiment, the same substance separates when the alkaline filtrate is acidified by acetic acid, and is in this case entirely free from the chief product of the reaction. The amount formed under the experimental conditions described is not more than 5 per cent., although the quantity is considerably increased if the temperature during the condensation is kept too high. It crystallises from alcohol in small needles, which melt at 212° , and yield malonic acid on complete alkaline hydrolysis. We have not as yet succeeded in assigning a satisfactory constitution to this substance.

3-Cyano-2: 6-diketo-4: 4-dimethylpiperidine-5-carboxylamide,



This compound is formed by the action of hot dilute hydrochloric acid on the piperidone base under the following conditions.

Ten grams of the base were suspended in 20 c.c. of water, and a sufficient quantity of hydrochloric acid was added to effect complete solution. The mixture was then raised to the boiling point, and kept at this temperature for one minute, when it was cooled and scratched with a glass rod. Crystals of the imide immediately

separated, which, when recrystallised from hot water, yielded long, colourless needles, melting and evolving gas at 250° :

0.1465 gave 0.2766 CO_2 and 0.0705 H_2O . $\text{C}=51.5$; $\text{H}=5.35$.

0.2238 „ 39.0 c.c. N_2 at 19° and 743 mm. $\text{N}=20.01$.

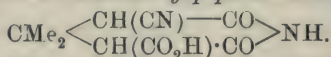
$\text{C}_9\text{H}_{11}\text{O}_3\text{N}_3$ requires $\text{C}=51.7$; $\text{H}=5.3$; $\text{N}=20.1$ per cent.

The imide dissolves in dilute aqueous sodium carbonate, forming a clear solution, from which a colourless *sodium* salt separates if the solution is concentrated. It is unchanged on prolonged boiling with water, but, when heated with aqueous sodium hydroxide, evolves ammonia, and is ultimately converted into $\beta\beta$ -dimethylglutarimide. The products formed on acid hydrolysis are the same as those produced from the piperidone base.

The Action of Hydrolysing Agents on 6-Imino-3-cyano-5-carbamyl-4:4-dimethylpiperidone.

(a) *Water.*

3-Cyano-2:6-diketo-4:4-dimethylpiperidine-5-carboxylic Acid,



When the imino-compound is boiled for a long time with water, ammonia is evolved, together with some acetone, and at the same time a small quantity of the di-imino-di-imide of $\beta\beta$ -dimethylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylic acid (see p. 435) is precipitated as colourless crystals. If the filtrate from these crystals is then boiled until free from ammonia, the solution, on evaporation, yields a gummy residue, which consists of a mixture of the above acid and its ammonium salt. The residue readily dissolves in water, and the solution, on being acidified by hydrochloric acid, deposits the above acid in colourless crystals. When recrystallised from water, it forms small prisms, which melt and evolve carbon dioxide at 221° :

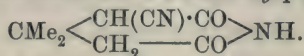
0.1344 gave 0.2518 CO_2 and 0.0591 H_2O . $\text{C}=51.21$; $\text{H}=4.91$.

0.1474 „ 17.1 c.c. N_2 at 14° and 738 mm. $\text{N}=13.46$.

$\text{C}_9\text{H}_{10}\text{O}_4\text{N}_2$ requires $\text{C}=51.4$; $\text{H}=4.8$; $\text{N}=13.3$ per cent.

The acid is characterised by giving a sparingly soluble *sodium* salt and *ammonium* salt. The former separates when sodium carbonate solution is added to a dilute aqueous solution of the acid.

3-Cyano-2:6-diketo-4:4-dimethylpiperidine,



When the nitrile-carboxylic acid described above is heated over its melting point until all carbon dioxide has ceased to be evolved,

an oil remains, which solidifies on cooling. When recrystallised from hot water, it forms long, colourless needles, melting at 200°. Owing to the high temperature required for this decomposition, the yield of the nitrile is not good; consequently it is better to prepare this substance by the action of dilute hydrochloric acid on 6-imino-3-cyano-5-carbamyl-4:4-dimethyl-2-piperidone. For this purpose, the piperidone derivative is dissolved in dilute hydrochloric acid (10 per cent.), and boiled for twelve hours. The product is filtered from a small quantity of the insoluble di-imide of $\beta\beta$ -dimethylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylic acid (see p. 436), and the filtrate evaporated to a small bulk. The crystals which separate are identical with those produced from the nitrile-carboxylic acid in the manner described above:

0.1685 gave 0.3548 CO_2 and 0.0917 H_2O . $\text{C}=57.41$; $\text{H}=6.10$.

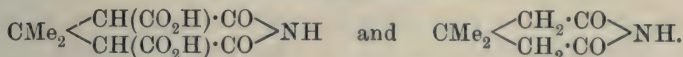
0.1181 „ 17.9 c.c. N_2 at 14° and 733 mm. $\text{N}=17.1$.

$\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$ requires $\text{C}=57.8$; $\text{H}=6.0$; $\text{N}=16.9$ per cent.

The nitrile slowly dissolves in aqueous sodium carbonate solution. Both the nitrile and its carboxylic acid pass into $\beta\beta$ -dimethylglutarimide when boiled with potassium hydroxide.

(b) Potassium Hydroxide.

The Imide of $\beta\beta$ -Dimethylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylic Acid and $\beta\beta$ -Dimethylglutarimide.



When the piperidone base is mixed with rather more than the calculated quantity of potassium hydroxide dissolved in water, a clear yellow solution is formed, from which the colour is discharged on warming, a change which is very clearly defined, and is due to the formation of the alkali salt of the double ring in a manner explained on p. 436. When the colourless solution is boiled, ammonia, together with some acetone, is evolved, and if the heating be continued until all ammonia has been driven off, for which purpose five hours are usually required, the solution will be found to contain the potassium salt of the above acid, together with $\beta\beta$ -dimethylglutarimide. The acid is best isolated by acidifying the solution with hydrochloric acid and evaporating to dryness with sand and ammonium sulphate, during which process a certain quantity of $\beta\beta$ -dimethylglutarimide, formed by the elimination of carbon dioxide from the dicarboxylic acid, sublimes on the sides of the vessel in long needles. The residue is then extracted in a Soxhlet apparatus with alcohol, and the alcoholic extract, after being evaporated to dryness, is mixed with ether. The dicarboxylic acid is quite

insoluble in ether, whereas the imide dissolves if a sufficient quantity of the solvent is used. Consequently, by repeatedly rubbing the residue with ether, the acid is ultimately obtained pure. It crystallises from water in small prisms, which melt and evolve carbon dioxide at 225—230°:

0.2001 gave 0.3463 CO_2 and 0.0882 H_2O . $\text{C}=47.21$; $\text{H}=4.88$.

$\text{C}_9\text{H}_{11}\text{O}_6\text{N}$ requires $\text{C}=47.3$; $\text{H}=4.8$ per cent.

The ethereal extract furnished a solid residue on evaporation; this crystallised from water in long needles, melting at 147°, which proved to be those of $\beta\beta$ -dimethylglutarimide. The amount of the imide formed in the hydrolysis depends on the length of the time during which the hydrolysis is allowed to proceed, and if the action is continued for a long time scarcely any of the dicarboxylic acid is formed. The imide is produced in quantitative yield when the dicarboxylic acid is distilled under ordinary pressure; its constitution was established by analysis (Found, $\text{C}=59.43$; $\text{H}=7.8$; silver salt $\text{Ag}=43.82$. Calc., $\text{C}=59.6$; $\text{H}=7.8$; silver salt $\text{Ag}=43.7$ per cent.), and its identity with $\beta\beta$ -dimethylglutarimide was proved by direct comparison with a specimen of this substance prepared from $\beta\beta$ -dimethylglutaric acid.

(c) *Mineral Acids*.—The action of hot dilute mineral acids, such as hydrochloric acid and sulphuric acid, on the piperidone derivative leads, as already mentioned, to the formation of the corresponding imide. Further action of the hot dilute acid then produces other changes, the reaction proceeding in two directions. One of these causes the ultimate hydrolysis of the compound to α -cyano- $\beta\beta$ -dimethylglutarimide (see p. 432); the other leads to the precipitation of the very insoluble di-imide of $\beta\beta$ -dimethylpropane- $\alpha\gamma\gamma$ -tetracarboxylic acid (see p. 436), which is not acted on by boiling with dilute acids. By far the greater quantity of the piperidone derivative follows the second direction, and if, therefore, a solution of the base in dilute sulphuric acid is boiled, the clear solution slowly deposits a crystalline precipitate of the di-imide, which is usually complete after three hours. When the filtrate from this compound is evaporated, it yields α -cyano- $\beta\beta$ -dimethylglutarimide (see p. 432).

$\beta\beta$ -Dimethylglutaric Acid.

As the processes described in this paper originated in a desire to prepare $\beta\beta$ -dimethylglutaric acid in quantity, it is advisable to describe the method by which we have succeeded in obtaining large amounts of this acid from the piperidone base.

One hundred grams of the base are placed in a litre flask, and mixed with 150 grams of concentrated sulphuric acid. Thirty c.c.

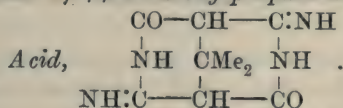
of water are then added to the hot solution, and the liquid heated on the sand-bath until the evolution of carbon dioxide, which is very vigorous, has ceased.

When this occurs, which is usually about one hour after the heating has been started, a further 50 c.c. of water are added, and the solution boiled on the sand-bath for five hours. It sometimes happens that owing to the sulphuric acid not being sufficiently strong, some separation of the insoluble di-imide takes place after the addition of the second quantity of water; this dissolves, however, on further heating.

A considerable quantity of acid separates from the acid solution on cooling, but it is advisable to add some water, saturate the solution with ammonium sulphate, and extract with ether, as a purer product is obtained in this manner than by filtering the strongly acid solution directly.

The acid prepared in this way possesses a high degree of purity, and can be at once used without further purification. The yield from the piperidone base is quantitative. The acid melted at 101° , and was characterised by analysis (Found, C=52.3; H=7.5. Calc., C=52.5; H=7.5 per cent.), and by the formation of its anhydride.

The Di-imino-di-imide of $\beta\beta$ -Dimethylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylic



This compound is produced from 6-imino-3-cyano-5-carbamyl-4:4-dimethyl-2-piperidone by the action of alkali, either in the form of sodium ethoxide or of sodium hydroxide. It is also formed, as already mentioned, as a by-product in the hydrolysis of the piperidone base by acids. The preparation by means of sodium ethoxide may be effected as follows: Ten grams of the finely-ground base are suspended in 75 c.c. of alcohol, and a solution containing 2.3 grams of sodium in 30 c.c. of alcohol is added. The addition of sodium ethoxide causes the base to dissolve, forming a clear yellow solution, from which, on warming on the water-bath, a colourless, crystalline sodium compound separates, and at the same time the yellow colour of the solution disappears. The sodium compound is then collected, washed with a little alcohol, and dried. The specimen analysed was dried at 80° , but the figures showed that it contained one molecule of alcohol of crystallisation:

0.3734 gave 0.1734 Na_2SO_4 . Na=15.1.

0.3306 „ 0.1546 Na_2SO_4 . Na=15.2.

$\text{C}_9\text{H}_{10}\text{O}_2\text{N}_4\text{Na}_2\cdot\text{C}_2\text{H}_6\text{O}$ requires Na=15.4 per cent.

It was not found possible to obtain a satisfactory analysis of the compound free from alcohol, as the temperature required to drive off the solvent caused appreciable decomposition of the salt.

The *sodium* salt is very deliquescent, and readily takes up moisture from the air. It dissolves in water, forming an alkaline solution, which, when acidified by acetic acid, deposits the base as a heavy, white precipitate, which is insoluble in all the usual solvents, and is best purified by dissolving in cold dilute hydrochloric acid and reprecipitating by the addition of sodium acetate solution. In this way it is obtained in small needles, which sublime at a high temperature without melting:

0.1555 gave 0.2929 CO_2 and 0.0844 H_2O . $\text{C}=51.41$; $\text{H}=6.01$.

0.1654 „, 38.2 c.c. N_2 at 20° and 750 mm. $\text{N}=26.66$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{N}_4$ requires $\text{C}=51.9$; $\text{H}=5.8$; $\text{N}=26.9$ per cent.

The di-imino-di-imide can also be formed by the aid of aqueous potassium hydroxide in the following way. Five grams of the piperidone base are dissolved in a sufficient quantity of dilute aqueous potassium hydroxide, and the clear yellow solution is warmed on the water-bath. After a few minutes, it becomes colourless, and if at this stage the solution is quickly cooled and acidified by acetic acid, the dicyclic base is precipitated. The end-point of the reaction is very clearly defined, and can be easily distinguished in daylight.

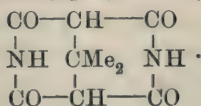
The compound is a di-acid base, and forms salts with two equivalents of hydrochloric acid. It dissolves in aqueous alkali, forming a colourless solution.

The *platinichloride* separates as lustrous, yellow plates when a solution of the base containing excess of hydrochloric acid is mixed with a solution of platinic chloride. The precipitation should be hastened by scratching, and the solution kept as cold as possible:

0.3944 gave 0.1238 Pt. $\text{Pt}=31.4$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{N}_4 \cdot \text{H}_2\text{PtCl}_6$ requires $\text{Pt}=31.5$ per cent.

The Di-imide of $\beta\beta$ -Dimethylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylic Acid,



When a solution of the di-imino-di-imide in dilute hydrochloric acid is warmed, the solution remains clear for a few minutes, and then slowly deposits glistening plates of the above compound. The same substance is also formed in small amount during the acid hydrolysis of the piperidone base in the manner already described.

It is insoluble in all the usual solvents, and sublimes at a high temperature without melting:

0.1384 gave 15.8 c.c. N_2 at 14° and 755 mm. $N=13.5$.

$C_9H_{10}O_4N_2$ requires $N=13.3$ per cent.

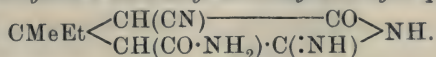
The compound is soluble in aqueous alkalis, and behaves in a characteristic manner when treated in ammoniacal solution with silver nitrate. Thus, when a solution in excess of ammonia is mixed with aqueous silver nitrate, a clear solution is formed, quickly changing to a clear transparent jelly, which slowly becomes opaque on keeping.

The Products of Hydrolysis of the Dicyclic Compounds described above.

As mentioned in the introduction, the second ring of the compounds described above is less stable towards hydrolysing agents than that of the single five-membered cyclic imides. Thus, when either the di-imino-di-imide or the di-imide is boiled with excess of aqueous alkali hydroxide, ammonia is evolved, and the ultimate product is $\beta\beta$ -dimethylglutarimide. No acetone is evolved during this hydrolysis, and the yield of the imide is practically quantitative. The compounds are not affected by aqueous alkali carbonates even on prolonged boiling. With acid hydrolysing agents, the hydrolysis is a matter of some difficulty, owing to the insolubility of the di-imide in all acids excepting concentrated sulphuric acid. Thus prolonged boiling with concentrated hydrochloric acid is without effect, and when the di-imino-di-imide is used, the clear solution, which is first formed, at once deposits the insoluble di-imide on warming. The only way to hydrolyse these compounds by acids is to use concentrated sulphuric acid, and to add only a very little water. The sulphuric acid should not be weaker than 85 per cent., and the clear solution should then be kept at about 150° until the evolution of carbon dioxide has ceased; more water may then be added, and the hydrolysis continued for five hours. In this way a quantitative yield of $\beta\beta$ -dimethylglutaric acid can be obtained.

The Condensation of Methyl Ethyl Ketone with Cyanoacetamide:

6-Imino-3-cyano-5-carbamyl-4-methyl-4-ethyl-2-piperidone,



This condensation was effected in much the same manner as described previously in the case of acetone, although, in this instance, the formation of the condensation product does not take place so readily, and the reaction requires a longer time. The conditions found to give the best results were as follows.

One hundred grams of cyanoacetamide were dissolved in a sufficient quantity of water, and mixed with 55 grams of methyl ethyl ketone. The solution was then warmed to 20° , and 1 c.c. of piperidine added. The clear yellow solution slowly deposited the piperidone base in colourless needles, the separation being complete after forty-eight hours, when the product was collected and dried. It was found to weigh 108 grams, and to be completely soluble in cold dilute hydrochloric acid. The filtrate deposited a further small quantity of crystalline material on keeping, which only partly dissolved in dilute hydrochloric acid. The soluble portion was therefore isolated by filtration, and the base precipitated from the solution by the addition of sodium acetate. In this way a further 8 grams were obtained. The base, as in the case of the corresponding acetone compound, is slowly decomposed by boiling water; it was therefore purified for analysis by dissolving in cold dilute hydrochloric acid, and precipitating from the filtered solution by the addition of sodium acetate. It is obtained in this way in lustrous plates, which melt and decompose at 225° :

0.1719 gave 0.3396 CO_2 and 0.0999 H_2O . $\text{C}=53.91$; $\text{H}=6.52$.

0.1639 „, 36.3 c.c. N_2 at 19° and 730 mm. $\text{N}=25.0$.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_4$ requires $\text{C}=54.0$; $\text{H}=6.3$; $\text{N}=25.2$ per cent.

The compound is a monacid base, and the hydrochloride separates in small needles when concentrated hydrochloric acid is added to a dilute solution of the salt.

The platinichloride separates in pale yellow plates when a solution of the base in excess of hydrochloric acid is mixed with platinic chloride solution:

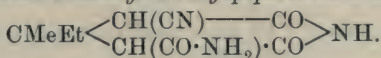
0.1812 gave 0.0411 Pt. $\text{Pt}=22.68$.

$(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$ requires $\text{Pt}=22.7$ per cent.

The piperidone base dissolves in aqueous potassium hydroxide, forming a yellow solution from which the colour is discharged on warming, a change which is due to the formation of the potassium salt of the di-imino-di-imide. Prolonged boiling with alkali hydroxide yields $\beta\beta$ -methylethylglutarimide, whilst complete hydrolysis with concentrated sulphuric acid furnishes a quantitative yield of $\beta\beta$ -methylethylglutaric acid.

The by-product corresponding with the substance melting at 212° formed in the acetone experiment is also produced in the present condensation, although in smaller quantity. It is separated from the piperidone base, as already described, by rubbing with dilute hydrochloric acid, and crystallises from alcohol in large, colourless prisms, which melt at 192° . As the analyses furnished no clue to the constitution of this substance, it was laid aside for further investigation.

3-Cyano-2: 6-diketo-4-methyl-4-ethylpiperidine-5-carboxylamide,



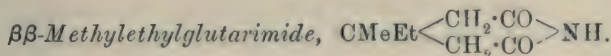
The conditions found most suitable for the preparation of this compound were the following. Ten grams of the base were dissolved in dilute hydrochloric acid, and the solution was heated to the boiling point for one minute. It was then cooled, and the crystals of the imide which separated were collected and recrystallised from water. It formed small prisms, melting and decomposing at 230—235°:

0.1306 gave 0.2540 CO₂ and 0.0711 H₂O. C=54.11; H=5.90.

0.1268 „, 20.3 c.c. N₂ at 17° and 743 mm. N=18.6.

C₁₀H₁₃O₃N₃ requires C=53.8; H=5.8; N=18.8 per cent.

The imide dissolves in dilute sodium carbonate solution. The products formed from it on hydrolysis are the same as those from the piperidone base.



This compound is formed as the ultimate product of hydrolysis of 6-imino-3-cyano-5-carbamyl-4-methyl-4-ethyl-2-piperidone, or the corresponding diketo-derivative, by aqueous potassium hydroxide. Either one or other of these compounds is boiled with an aqueous solution containing rather more than the calculated quantity of potassium hydroxide until the odour of ammonia ceases to be apparent, when the solution is acidified by hydrochloric acid, saturated with ammonium sulphate, and extracted several times with ether. The oily residue left on evaporating the ether is then heated at 160° until the evolution of carbon dioxide has ceased, when the residue, which solidifies on cooling, is recrystallised from water. *ββ-Methylethylglutarimide* forms lustrous plates, which melt at 127°:

0.1446 gave 0.3269 CO₂ and 0.1095 H₂O. C=61.72; H=8.41.

C₈H₁₃O₂N requires C=61.9; H=8.4 per cent.

The imide is sparingly soluble in cold ether, and can be recrystallised from this solvent; it can also be recrystallised from benzene.

The *silver* salt separates as a colourless precipitate when a little ammonia is added to a solution of the compound in dilute silver nitrate solution:

0.2465 gave 0.1015 Ag. Ag=41.18.

C₈H₁₂O₂NAg requires Ag=41.2 per cent.

ββ-Methylethylglutaric Acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

This acid is produced in quantitative yield when the piperidone base or the corresponding imide is heated with 70 per cent. sulphuric acid. Fifty grams of the base are dissolved in 75 c.c. of concentrated sulphuric acid, and 25 c.c. of water are added to the hot solution. The mixture is then quickly heated on the sand-bath until carbon dioxide begins to be evolved, when it is maintained at this temperature until all gas has been given off. A further 30 c.c. of water are then added, and the heating continued for five hours. If too much water is added in the first instance, a crystalline precipitate of the di-imide separates on heating, and when once this compound has separated, it will not again dissolve. The acid is extracted from the cooled product of hydrolysis by means of ether, and is obtained as a crystalline mass on evaporating the dried ethereal solution. The acid is sufficiently pure for general purposes, but can be recrystallised from a mixture of equal parts of concentrated hydrochloric acid and water, from which it separates in striated, fan-shaped needles. The specimen for analysis was recrystallised from benzene and obtained in long needles, melting at 86° :

0.1794 gave 0.3627 CO_2 and 0.1308 H_2O . $\text{C}=55.10$; $\text{H}=8.11$.

$\text{C}_8\text{H}_{14}\text{O}_4$ requires $\text{C}=55.2$; $\text{H}=8.0$ per cent.

ββ-Methylethylglutaric Anhydride, $\text{CMeEt}\begin{matrix} \text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO} \end{matrix}\text{O}$.

This compound may be prepared either by the action of acetyl chloride or acetic anhydride on the acid. Ten grams are dissolved in the dehydrating agent, and heated to the boiling point for one hour. The solution is then distilled, first under ordinary pressure until free from acetic acid, and then under diminished pressure. The anhydride distils as a clear, colourless liquid at $185^\circ/20$ mm. It could not be obtained in a solid condition:

0.2477 gave 0.5570 CO_2 and 0.1711 H_2O . $\text{C}=61.25$; $\text{H}=7.72$.

$\text{C}_8\text{H}_{12}\text{O}_3$ requires $\text{C}=61.5$; $\text{H}=7.7$ per cent.

The anhydride slowly dissolves on boiling with water, regenerating the acid from which it was derived.

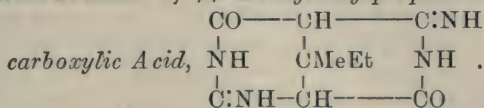
The *α-naphthylamic acid*, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is prepared by boiling a solution of the anhydride in benzene with a solution of *α*-naphthylamine in the same solvent and evaporating the solution to dryness. The viscid oil which remains solidifies on being rubbed with dilute hydrochloric acid. It crystallises from alcohol in long needles, melting at 126° :

0.1676 gave 0.4416 CO_2 and 0.1060 H_2O . $\text{C}=71.81$; $\text{H}=7.00$.

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{C}=71.6$; $\text{H}=6.7$ per cent.

Derivatives of the anhydride seem to possess little tendency to crystallise, and the anilic acid from the anhydride and aniline, as well as the toluic acids from the three toluidines, could only be obtained as oils.

The Di-imino-di-imide of $\beta\beta$ -Methylethylpropane- $\alpha\alpha\gamma\gamma$ -tetra-



As in the case of the compound formed in the acetone condensation, this substance may be prepared from the piperidone base either by the action of sodium ethoxide or by the aid of aqueous sodium hydroxide. In the experiment with sodium ethoxide, 7 grams of the finely ground base were suspended in 25 c.c. of alcohol and mixed with a solution containing 1.5 grams of sodium in 20 c.c. of alcohol. The base dissolved on adding the alkali, forming a yellow solution, from which a colourless, crystalline sodium salt separated on warming. This salt was collected, dissolved in water, and the solution rendered acid by acetic acid, when a copious precipitate of the di-imino-base ensued. The same substance may also be produced in the following way. The piperidone base is dissolved in a sufficient quantity of dilute aqueous potassium hydroxide, and the yellow solution is then gently warmed until the colour is discharged, when it is immediately cooled and rendered acid by acetic acid. The di-imino-base is then precipitated in the pure condition.

It is very sparingly soluble in all the usual solvents, and is therefore best purified for analysis by dissolving in cold dilute hydrochloric acid, and reprecipitating from the filtered solution by the addition of sodium acetate solution. In this way it is obtained in small, colourless needles, which melt and decompose at 294° :

0.1496 gave 32.7 c.c. N_2 at 12° and 726 mm. $\text{N}=25.1$.

0.1494 „ 32.4 c.c. N_2 „ 13° „ 739 mm. $\text{N}=25.2$.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_4$ requires $\text{N}=25.2$ per cent.

It is worthy of remark that several carbon and hydrogen estimations of this substance invariably gave the carbon content as 2 per cent. too low. As the combustions were carried out both in copper oxide and lead chromate tubes, the loss of carbon can be hardly due to the formation of paraffin hydrocarbons, but must be ascribed to incomplete combustion.

The di-imino-di-imide dissolves in aqueous alkali hydroxide, form-

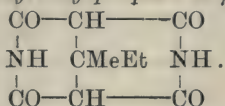
ing a colourless solution, and forms a salt with hydrochloric acid containing two equivalents of the acid.

The *platinichloride* requires some care in preparation, owing to the ease with which the base is hydrolysed to the di-imide even by cold dilute hydrochloric acid. It separates in yellow plates from a concentrated solution of the base, containing as little hydrochloric acid as possible, when it is mixed with an aqueous solution of platinic chloride:

0.4273 gave 0.1333 Pt. $\text{Pt} = 31.19$.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_4, \text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 30.9$ per cent.

The Di-imide of $\beta\beta$ -Methylethylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylic Acid,



This compound separates in glistening plates when a solution of the di-imino-base in dilute hydrochloric acid is gently warmed. When prepared in this manner, it is quite free from all impurities, although it may be recrystallised from a considerable quantity of hot alcohol. It melts and darkens at $330\text{--}331^\circ$ (corr.): *

0.1988 gave 0.3896 CO_2 and 0.0935 H_2O . $\text{C} = 53.41$; $\text{H} = 5.20$.

0.1369 „ 15.0 c.c. N_2 at 13° and 745 mm. $\text{N} = 12.7$.

$\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$ requires $\text{C} = 53.6$; $\text{H} = 5.3$; $\text{N} = 12.5$ per cent.

The di-imide dissolves slowly in an aqueous solution of sodium carbonate.

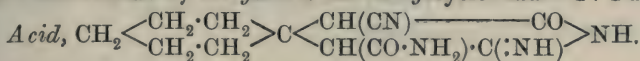
The Silver Salt.—When silver nitrate solution is added to a solution of the di-imide in excess of ammonia, a white precipitate is formed, which again passes into solution. When the containing vessel is scratched, a crystalline salt separates. Care must be taken in this preparation to have excess of ammonia present; otherwise a gelatinous silver salt separates:

0.1438 gave 0.0467 Ag. $\text{Ag} = 32.47$.

$\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_2\text{Ag}$ requires $\text{Ag} = 32.7$ per cent.

The products formed by the hydrolysis of the di-imino-base and the di-imide are similar to those from the corresponding compounds formed in the acetone condensation. Thus, on complete hydrolysis with aqueous alkali hydroxide, $\beta\beta$ -methylethylglutarimide is formed, and when they are boiled with concentrated sulphuric acid, a quantitative yield of $\beta\beta$ -methylethylglutaric acid is obtained. The conditions required are the same as those given in the case of the acetone compounds.

* Melting points above 300° were taken in cyanobenzylene (compare Trans., 1906, 89, 1932).

*The Condensation of cycloHexanone with Cyanoacetamide.**The ω'-Imino-imide of α-Cyano-α'-carbamylicyclohexane-1:1-diacetic*

Owing to the insolubility of *cyclohexanone* in water, it is necessary in this condensation to use alcohol in order to bring the reacting substances into solution. Seventy-four grams of cyanoacetamide were dissolved in a sufficient quantity of cold water, and 44 grams of *cyclohexanone*, together with sufficient alcohol to ensure complete solution, added. The addition of 1 c.c. of piperidine or of 1 c.c. of 30 per cent. sodium hydroxide solution caused the liquid to become yellow, and at the end of twelve hours a large quantity of crystalline material had separated. When collected and dried, the product weighed 90 grams, and was found to be completely soluble in dilute hydrochloric acid. A further quantity of crystalline substance separated from the filtrate on keeping, and 8 grams more of the base were obtained on rubbing this with dilute hydrochloric acid, filtering, and adding sodium acetate solution to the filtrate. The base, like the other compounds of this class, is slowly decomposed on boiling with water, and it is therefore best to purify it by dissolving in dilute hydrochloric acid, filtering, and precipitating the base by sodium acetate solution. It is obtained in this way in microscopic needles, which melt and decompose at 305°:

0.1810 gave 0.3841 CO₂ and 0.1050 H₂O. C=57.93; H=6.51.

0.1183 „ 23.6 c.c. N₂ at 16° and 733 mm. N=22.8.

C₁₂H₁₆O₂N₄ requires C=58.1; H=6.4; N=22.6 per cent.

The base is readily soluble in dilute mineral acids, and dissolves in aqueous sodium hydroxide, forming a yellow solution, from which the colour is discharged on warming, a change which is due to the formation of the disodium salt of the di-imino-di-imide. Complete hydrolysis with alkali hydroxide yields the imide of *cyclohexane-1:1-dimalonic acid*, whilst ultimate hydrolysis with concentrated sulphuric acid furnishes a quantitative yield of *cyclohexane-1:1-diacetic acid*.

The *platinichloride* separates as a yellow precipitate when a solution of the base in dilute hydrochloric acid is mixed with a solution of platinic chloride:

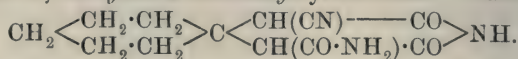
0.3217 gave 0.0686 Pt. Pt=21.32.

(C₁₂H₁₆O₂N₄)₂.H₂PtCl₆ requires Pt=21.5 per cent.

As in the former condensations, a small quantity of a second substance, insoluble in dilute hydrochloric acid, is formed during the condensation of *cyclohexanone* with cyanoacetamide. It occurs only in the later stages, and is isolated in the same manner as the

analogous compounds from the previous condensations. It separates from alcohol in small, colourless needles, which melt at 207°. We have not as yet succeeded in assigning any satisfactory constitution to this substance.

The ω-Imide of α-Cyano-α'-carbamylcyclohexane-1:1-diacetic Acid,



This substance is formed when the base already described is warmed with dilute hydrochloric acid. Ten grams of the base are dissolved in a sufficient quantity of dilute hydrochloric acid, and the solution is then raised to the boiling point and maintained at this temperature for one minute. Crystals of the imide separate on cooling. It can be recrystallised from alcohol, and is obtained in colourless prisms, melting sharply to an opaque liquid at 260°, which clears and decomposes at 300°:

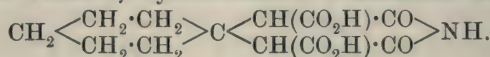
0.1722 gave 0.3639 CO₂ and 0.0926 H₂O. C=57.73; H=6.04.

0.1136 „, 17.6 c.c. N₂ at 23° and 725 mm. N=17.1.

C₁₂H₁₅O₃N₃ requires C=57.8; H=6.0; N=16.9 per cent.

The imide slowly dissolves in sodium carbonate solution. The products formed on hydrolysis are the same as those from the imino-imide.

The Imide of cycloHexane-1:1-dimalonic Acid,



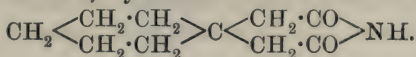
This compound is produced when either the imino-imide or the imide is boiled with aqueous alkali hydroxide. A convenient quantity is dissolved in an aqueous solution containing rather more than the calculated quantity of potassium hydroxide, and boiled until the odour of ammonia ceases to be apparent, when it is filtered and acidified with hydrochloric acid. Crystals of the acid slowly separate, which, when recrystallised from water, yield small needles, melting at 117°; the liquid evolves carbon dioxide a few degrees higher, and then re-solidifies. This change is due to the passage of the dicarboxylic acid into the imide, which melts at 168°:

0.1901 gave 0.3724 CO₂ and 0.0975 H₂O. C=53.42; H=5.70.

C₁₂H₁₅O₆N requires C=53.5; H=5.6 per cent.

The acid is very sparingly soluble in ether.

The Imide of cycloHexane-1 : 1-diacetic Acid,



The imide-dicarboxylic acid, when heated in a bath of sulphuric acid at 180° until the evolution of carbon dioxide has ceased, leaves the imide as an oily residue, which solidifies on cooling. It crystallises from benzene in large, prismatic needles, which melt at 168° :

0.2186 gave 0.5286 CO_2 and 0.1582 H_2O . $\text{C} = 66.01$; $\text{H} = 8.10$.

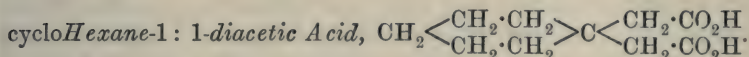
$\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C} = 66.2$; $\text{H} = 8.3$ per cent.

The imide is very sparingly soluble in ether or water.

The *silver* salt separates from a solution of the imide in excess of ammonia on the addition of silver nitrate solution as a colourless, crystalline precipitate:

0.3002 gave 0.1120 Ag. $\text{Ag} = 37.30$.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{NAg}$ requires $\text{Ag} = 37.5$ per cent.



The conversion of the ω' -imino-imide of α -cyano- α' -carbamyl-*cyclohexane-1 : 1-diacetic acid* into the above acid is accomplished, as in the former cases, by the aid of concentrated sulphuric acid. Forty grams of the imino-imide are dissolved in 100 c.c. of concentrated sulphuric acid, and the warm solution mixed with 15 c.c. of water. It is then heated on the sand-bath until carbon dioxide begins to be evolved, when it is kept at about this temperature until all has been given off, which is usually at the end of one hour. A further 50 c.c. of water are then added, and the solution boiled for five hours. If some of the crystalline di-imide separates during the process of hydrolysis, which is always the case if too much water has been added, it is advisable to filter it off through glass wool, as when once it has separated, it will not redissolve on further heating. If, however, the conditions given above are carefully followed, the di-imide will not separate, and the hydrolysis will be complete. Although the acid separates from the sulphuric acid solution on cooling, it is advisable to extract with ether and shake the ethereal solution with aqueous sodium carbonate, the acid being precipitated from the alkaline extract by means of hydrochloric acid.

cycloHexane-1 : 1-diacetic acid crystallises from dry ether in small, colourless prisms, which melt at 181° . It is sparingly soluble in hot water, but can be recrystallised from this solvent if a sufficient quantity is used. For general purposes it is conveniently

recrystallised from dilute alcohol. It is sparingly soluble in benzene. When distilled under ordinary pressure, it passes into the anhydride, the change being effected without any charring:

0.2159 gave 0.4742 CO_2 and 0.1539 H_2O . $\text{C}=59.92$; $\text{H}=7.93$.

$\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C}=60.01$; $\text{H}=8.0$ per cent.

A neutral solution of the ammonium salt of the acid gives a green, crystalline precipitate with copper sulphate, a white, crystalline precipitate on boiling with calcium chloride, and a heavy, white precipitate with lead acetate. The *barium* salt is soluble.

The *silver* salt separates as a colourless, crystalline precipitate on adding a solution containing the calculated quantity of silver nitrate to a neutral solution of the ammonium salt of the acid:

0.2383 gave 0.1239 Ag . $\text{Ag}=52.02$.

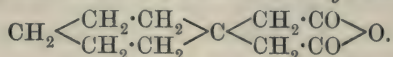
$\text{C}_{10}\text{H}_{14}\text{O}_4\text{Ag}_2$ requires $\text{Ag}=52.2$ per cent.

The *diethyl* ester is formed when a solution of the acid in alcohol is mixed with one-third of its volume of concentrated sulphuric acid, and heated for one hour on the water-bath. It is extracted by pouring the product into water and separating the oil by means of ether, the ethereal solution being subsequently washed with sodium carbonate, dried, and evaporated. The ester distils at $288^\circ/733$ mm., without any decomposition, as a clear, mobile liquid:

0.1691 gave 0.4061 CO_2 and 0.1410 H_2O . $\text{C}=65.50$; $\text{H}=9.32$.

$\text{C}_{14}\text{H}_{24}\text{O}_4$ requires $\text{C}=65.6$; $\text{H}=9.4$ per cent.

cycloHexane-1: 1-diacetic Anhydride,



This substance is formed either by the action of acetyl chloride or of acetic anhydride on the acid. For the preparation of large quantities; acetic anhydride is preferable, and it is only necessary to boil a solution of the acid in excess of anhydride for two hours and to distil the product in order to obtain the anhydride in a pure condition. It distils without decomposition at $329^\circ/743$ mm. and $213^\circ/36$ mm. as a colourless liquid, which solidifies on cooling. It then crystallises from a mixture of light petroleum (b. p. $80-90^\circ$) and benzene in fine, silky needles, which melt at 73° :

0.2165 gave 0.5230 CO_2 and 0.1436 H_2O . $\text{C}=65.91$; $\text{H}=7.45$.

$\text{C}_{10}\text{H}_{14}\text{O}_3$ requires $\text{C}=65.9$; $\text{H}=7.7$ per cent.

The anhydride dissolves when warmed with aqueous alkali, and the solution, on acidifying, deposits the acid melting at 181° .

The *anilic acid* is prepared by mixing a solution of the anhydride in benzene with a benzene solution of aniline, and raising the mixture to the boiling point. It is isolated by evaporating the

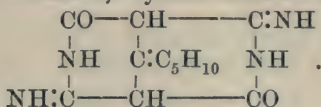
solution until free from benzene, and rubbing the residue with dilute hydrochloric acid. The solid which is then formed crystallises from dilute alcohol in glistening plates, which melt at 146° :

0.1514 gave 0.3864 CO_2 and 0.1045 H_2O . $\text{C}=69.60$; $\text{H}=7.71$.

$\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=69.8$; $\text{H}=7.6$ per cent.

The anilic acid is readily soluble in benzene and in alcohol.

The Di-imino-di-imide of cycloHexane-1:1-dimalonic Acid,



The methods used for the preparation of this substance were essentially the same as those employed for the production of the similar compounds in the earlier condensations.

By Sodium Ethoxide.—12.4 Grams of the base were suspended in 40 c.c. of alcohol and mixed with a solution containing 2.3 grams of sodium in 30 c.c. of alcohol. The yellow solution which was then formed deposited, on warming, a large quantity of a colourless, crystalline sodium compound, which was collected, washed with alcohol, and dried:

0.3762 gave 0.1561 Na_2SO_4 . $\text{Na}=13.44$.

$\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_4\text{Na}_2, \text{C}_2\text{H}_6\text{O}$ requires $\text{Na}=13.6$ per cent.

It was not found possible to free the sodium compound from alcohol without causing decomposition. The salt is readily soluble in cold water, and when the solution is rendered acid by acetic acid, a colourless precipitate of the di-imino-base ensues.

By Alkali Hydroxide.—When the ω' -imino-imide of α -cyano- α' -carbamylocyclohexane-1:1-diacetic acid is dissolved in a sufficient quantity of aqueous potassium hydroxide, a yellow solution is formed, which, on warming, becomes colourless. If the solution is at this stage rapidly cooled and acidified by acetic acid, the di-imino-base is at once precipitated. The di-imino-di-imide is insoluble in all the usual organic solvents, but can be purified by dissolving in cold dilute hydrochloric acid, and reprecipitating by the addition of sodium acetate solution. It forms a micro-crystalline powder, which melts and decomposes at 303° :

0.1445 gave 28.6 c.c. N_2 at 15° and 726 mm. $\text{N}=22.5$.

$\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_4$ requires $\text{N}=22.6$ per cent.

We were unable to obtain a satisfactory carbon estimation of this compound, for, as in the case of the corresponding compound from methyl ethyl ketone, the figures were always from 1 to 2 per cent. too low.

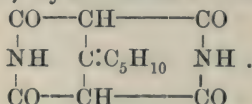
The di-imino-di-imide dissolves in aqueous potassium hydroxide, forming a colourless solution, and gives with hydrochloric acid a salt which contains two equivalents of the acid.

The *platinichloride* separates as a yellow precipitate when a solution of platinic chloride is added to a cold solution of the base in dilute hydrochloric acid:

0.3748 gave 0.1104 Pt. $Pt = 29.45$.

$C_{12}H_{14}O_2N_4 \cdot H_2PtCl_6$ requires $Pt = 29.6$ per cent.

The Di-imide of cycloHexane-1:1-dimalonic Acid,



This substance is formed when a solution of the di-imino-base in dilute hydrochloric acid is boiled for one minute, and separates completely from the hot solution. It can be recrystallised from much glacial acetic acid, and separates in small prisms, which melt at $400-405^\circ$, partly subliming below that temperature:

0.1904 gave 0.4030 CO_2 and 0.0932 H_2O . $C = 57.83$; $H = 5.50$.

0.1236 „ 12.0 c.c. N_2 at 14° and 748 mm. $N = 11.45$.

$C_{12}H_{14}O_4N_2$ requires $C = 57.6$; $H = 5.6$; $N = 11.2$ per cent.

The di-imide dissolves in a warm solution of sodium carbonate.

The products of hydrolysis of the di-imino-base and the di-imide are the same as those from the corresponding monocyclic compounds. Thus, with alkali hydroxide, the imide of *cyclohexane-1:1-diacetic acid* is the ultimate product, whilst with concentrated sulphuric acid a quantitative yield of *cyclohexane-1:1-diacetic acid* is obtained.

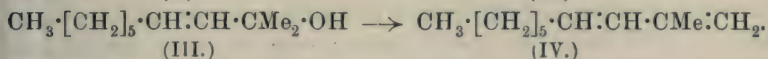
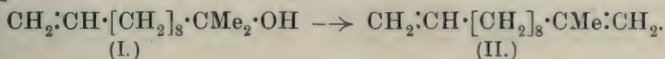
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THE UNIVERSITY, SHEFFIELD.

LIV.— β -Methyl- Δ^{α} -dodecadiene and β -Methyl- $\Delta^{\alpha\gamma}$ -decadiene.

By VICTOR JOHN HARDING, GERTRUDE MAUD WALSH, and
CHARLES WEIZMANN.

THE compounds described in this communication were prepared with a view to their possible technical importance, and although some of the substances possess some value as perfumes, their pro-

duction by the methods described here render them too costly to permit of their technical application. β -Methyl- $\Delta^{a\lambda}$ -dodecadiene and β -methyl- $\Delta^{a\gamma}$ -decadiene were prepared by the withdrawal of water from the corresponding tertiary alcohols, it being assumed that they possess the constitution indicated:



The tertiary alcohols were obtained by the action of the Grignard reagent on methyl undecenoate and methyl nonenoate respectively. The removal of water from (I) was easily effected by means of phthalic anhydride, but the second alcohol (III), on treatment with any acid dehydrating agent, gave polymerised products of high boiling point, and anhydrous baryta had no action. By allowing the Grignard mixture to remain for twenty-four hours, however, water was eliminated, and the hydrocarbons were obtained, although in extremely poor yield. Another interesting compound, namely, *methyl θ -aldehydo-n-nonoate*, $\text{CHO} \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{Me}$, was obtained by the action of ozone on methyl undecenoate.

EXPERIMENTAL.

aa-Dimethyl- Δ^x -undecenyl Alcohol, $\text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_8 \cdot \text{CMe}_2 \cdot \text{OH}$.

Fifty grams of magnesium methyl iodide were prepared in ethereal solution in the usual manner, and to the solution were added 30 grams of methyl undecenoate, also in ethereal solution, the flask being kept cold by a stream of water. The product was decomposed by water and hydrochloric acid, the ethereal layer separated, washed with water, and ether removed by distillation. The residual oil was then boiled for ten minutes with alcoholic potassium hydroxide to destroy any unchanged ester, and poured into water. The alcohol, which separated as an oil, was extracted with ether, dried over anhydrous magnesium sulphate,* and distilled. It is a colourless oil, with a characteristic and rather unpleasant odour, and boils at $130^\circ/10$ mm.:

0.1432 gave 0.4134 CO_2 and 0.1718 H_2O . $\text{C}=78.7$; $\text{H}=13.3$.

$\text{C}_{13}\text{H}_{26}\text{O}$ requires $\text{C}=78.8$; $\text{H}=13.1$ per cent.

Determination of the refractive power gave: $t=22.2^\circ$; $D_4^{22.2}$ 0.84217; M_d 62.54; M_β 63.68; M_γ 64.24; $M_\gamma - M_d = 1.7$;

$$\left(M = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{p}{a} \right).$$

* For drying alcohols in ethereal solution it has been found that anhydrous magnesium sulphate is much preferable to the more commonly used sodium sulphate.

β -Methyl- $\Delta^{\alpha\lambda}$ -dodecadiene, $\text{CH}_3 \cdot \text{CH} \cdot [\text{CH}_2]_8 \cdot \text{CMe} \cdot \text{CH}_2$.

This hydrocarbon is easily and quantitatively prepared from the above-mentioned alcohol by boiling it with the theoretical quantity of phthalic anhydride for four hours. The mixture is then poured into a dilute solution of sodium carbonate, the hydrocarbon extracted by means of ether, and distilled, when it passed over at $150\text{--}155^\circ/67$ mm. On redistillation over metallic sodium, the hydrocarbon boiled at $152^\circ/67$ mm.:

0.1267 gave 0.3999 CO_2 and 0.1518 H_2O . $\text{C} = 86.1$; $\text{H} = 13.3$.

$\text{C}_{13}\text{H}_{24}$ requires $\text{C} = 86.6$; $\text{H} = 13.3$ per cent.

β -Methyl- $\Delta^{\alpha\lambda}$ -dodecadiene is a colourless oil with a faint, lemon-like odour.

$\alpha\alpha$ -Dimethyl- Δ^{β} -nonenyl Alcohol, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{CMe}_2 \cdot \text{OH}$, and

β -Methyl- $\Delta^{\alpha\gamma}$ -decadiene, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}_2$.

Both these substances can be prepared by the interaction of magnesium methyl iodide and methyl Δ^{α} -nonenoate (compare Harding and Weizmann, Trans., 1910, **97**, 299). To prepare the alcohol, methyl Δ^{α} -nonenoate is added to the theoretical amount of magnesium methyl iodide in ethereal solution. After two hours, the product is worked up in the usual way. The yield is about 30 per cent. of the theoretical. The alcohol boils at $88\text{--}90^\circ/10$ mm., and possesses an odour resembling that of *n*-nonaldehyde:

0.1325 gave 0.3778 CO_2 and 0.1514 H_2O . $\text{C} = 77.7$; $\text{H} = 12.7$.

$\text{C}_{11}\text{H}_{22}\text{O}$ requires $\text{C} = 77.6$; $\text{H} = 12.9$ per cent.

Determination of refractive power gave: $t = 17.7^\circ$; $D_4^{17.7} 0.8265$; $M_\alpha 54.38$; $M_\beta 55.46$; $M_\gamma 55.92$; $M_\gamma - M_\alpha = 1.54$.

The compound can be boiled unchanged over anhydrous baryta, but when treated with dehydrating agents, such as phthalic anhydride, zinc chloride, or potassium hydrogen sulphate, polymerised products of high boiling point are obtained.

β -Methyl- $\Delta^{\alpha\gamma}$ -decadiene is obtained if the mixture of methyl Δ^{α} -nonenoate and magnesium methyl iodide is allowed to remain for twenty-four hours. The yield is, however, extremely poor. The hydrocarbon is purified by repeated distillation over sodium, and boils at 184° :

0.1834 gave 0.5802 CO_2 and 0.2091 H_2O . $\text{C} = 86.2$; $\text{H} = 12.7$.

$\text{C}_{11}\text{H}_{20}$ requires $\text{C} = 86.8$; $\text{H} = 13.1$ per cent.

By the interaction of magnesium methyl iodide and methyl crotonate under similar conditions, a small quantity of ethyl alcohol was obtained, and a second fraction, distilling at $122\text{--}124^\circ$, con-

sisted of methylethylisopropylcarbinol. (Found, $C=72.5$; $H=14.4$. Calc., $C=72.4$; $H=13.8$ per cent.)

Determination of the refractive power in ethyl-alcoholic solution gave $t=20.4^{\circ}$; $D_4^{20.4} 0.8101$; M_a of solute $=36.41$.

Methyl θ -Aldehyde-n-nonoate, $CO_2Me \cdot [CH_2]_8 \cdot CHO$.

This aldehyde was prepared by passing a current of ozonised oxygen through a solution of methyl undecenoate in chloroform, covered by a layer of water, until the ozone ceased to be absorbed. The chloroform solution was then shaken with a solution of sodium hydrogen sulphite, and the sodium hydrogen sulphite compound, which separated out after some time, collected, washed with ether, and freed from the remainder of the adhering oil by porous porcelain. The colourless, lustrous solid was then distilled in a current of steam from very dilute sodium carbonate solution, and the small amount of oil which passed over was converted into the semicarbazone, which crystallised from alcohol in small needles, melting at $94-96^{\circ}$:

0.1309 gave 0.2735 CO_2 and 0.1066 H_2O . $C=57.0$; $H=9.0$.

$C_{13}H_{25}O_3N_3$ requires $C=57.6$; $H=9.2$ per cent.

The aldehyde-acid, which possesses a very agreeable, fruity odour, was liberated from its semicarbazone by warm dilute hydrochloric acid.

THE UNIVERSITY,
MANCHESTER.

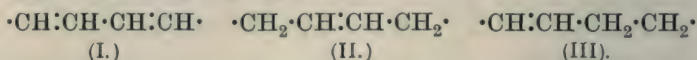
LV.—*The Influence of Conjugated Linkings on General Absorptive Power. Part I. The Absorption Spectra of Some Benzene Derivatives.*

By CECIL REGINALD CRYMBLE, ALFRED WALTER STEWART,
ROBERT WRIGHT, and WILLIAM GERALD GLENDINNING.

WHEN an attempt is made to classify the various types of absorption spectra, the first distinction which is drawn is between what is termed general absorption and selective absorption: that is, compounds are divided into those which show a banded absorption spectrum and those which, showing no banded absorption, merely allow more and more of the spectrum to pass through their solutions as the latter are diluted. At the first glance, these two types appear to be quite distinct from one another, but further consideration will show that general absorption may be merely a

special case of selective absorption in which the apparatus devised up to the present is not sufficiently sensitive to detect the other side of the band. For instance, the ordinary photographic plate is sensitive up to a frequency of between four and five thousand; but if the head of a band in any substance lay beyond this region, we should have no means of determining its position, and consequently we should assume that the substance in question gave merely general absorption. The only method which seems likely to throw light on the problem is to study the influences which affect general and selective absorption with a view to correlate the two types. The present paper represents an attempt to determine the influence of unsaturated groupings in the molecule on general absorption.

It was shown by Thiele (*Annalen*, 1899, **306**, 87) that the grouping (I), on reduction, yielded a grouping (II), and not, as was expected, the grouping (III):



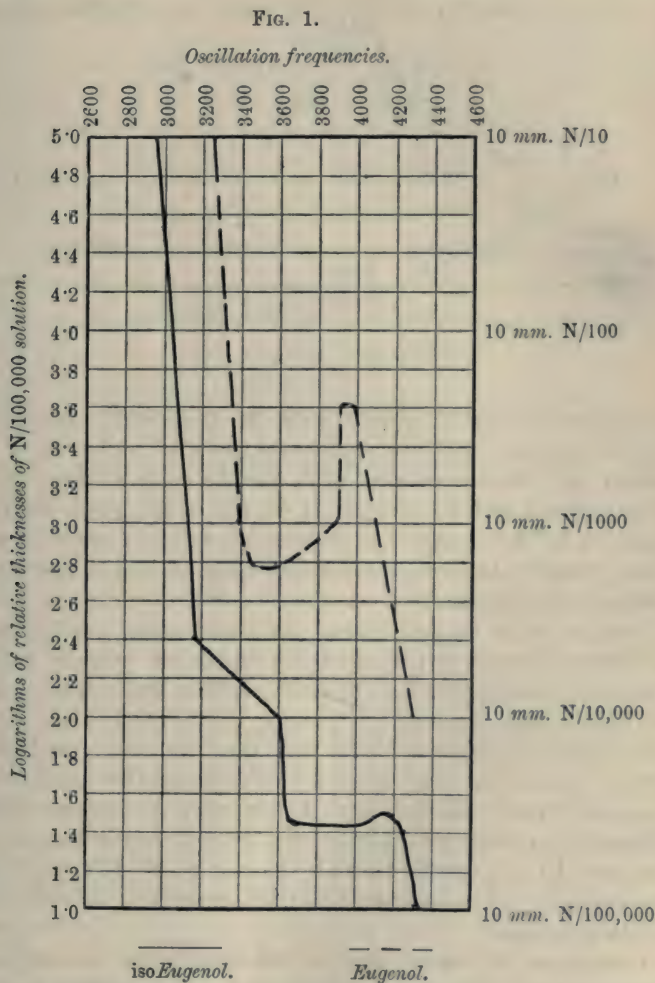
and to explain this he put forward his "partial valency" hypothesis, in which he assumed that the affinities of the carbon atoms on either side of the double bonds are not completely saturated, but that there remain partial valencies which, remaining free, are ready to attach themselves to fresh atoms outside the system. The two partial valencies on either side of the central single bond are supposed mutually to saturate each other and thus become temporarily inactive.

It has been shown by Brühl (*Ber.*, 1907, **40**, 878) that such a grouping has a strong influence on refractive power, producing higher values than the calculated refractivity. Hilditch (*Trans.*, 1909, **95**, 331, 1570, 1578; 1910, **97**, 1091; Edminson and Hilditch, *ibid.*, 1910, **97**, 223) has traced the same influence in the case of optically active substances. Analogous results were observed by Pascal (*Compt. rend.*, 1909, **149**, 342) in the case of diamagnetic power. Sir W. H. Perkin (*Trans.*, 1896, **69**, 1141) proved that a similar effect was noticeable in the case of magnetic rotation. One of the present authors, in conjunction with Professor Baly, drew attention to the fact that two conjugated carbonyl groups had a very marked influence on absorption spectra, an absorption band being developed in the spectra of compounds which contain such a grouping.

Bearing the foregoing in mind, it seemed desirable to turn to the question of general absorption and examine the spectra of various isomerides which contained systems of one or more conjugated double bonds, with a view to determine the effect which

the presence of the conjugation produced on the absorptive power of the substances. The present paper contains an account of the investigation of some benzene derivatives.

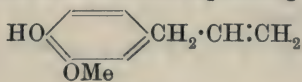
It is clear that comparisons can only be made between two sets



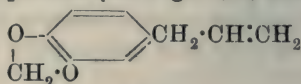
of isomeric substances; since the carbon atom in itself appears to exert a certain absorptive power, it would not be proper to compare the general absorptions of two substances one of which contained more atoms than the other.

In the first place, we may consider a group of six compounds

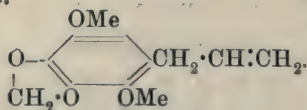
which are closely allied to one another, namely, eugenol, safrole, and apiole, with the corresponding *iso*-compounds (see Figs. 1, 2, and 3):



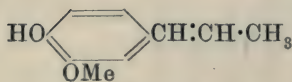
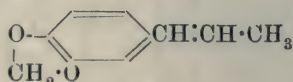
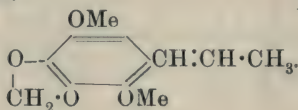
Eugenol.



Safrole.



Apiole.

*iso*Eugenol.*iso*Safrole.*iso*Apiole.

An examination of the six formulæ above will show that in the case of eugenol and its analogues the double bonds in the side chains are not conjugated with the benzene nuclei; in the case of *isoeugenol* and its congeners, on the other hand, an extra conjugation is introduced, for the double bond in the side chain has been brought nearer to the benzene nucleus, and is now part of the conjugated system.

Turning now to the curves, we must make a selection of the particular region of the spectrum which we propose to examine. As we are dealing with general absorption, it is quite evident that we should not examine the portion of the spectrum which forms part of an absorption band, but that we must deal with some section which lies sufficiently far away from the banded region to be secure from interference on the part of factors which exert influence on selective absorption. If we choose the region lying between 10 mm. of *N*/10 and 10 mm. of *N*/100, we shall avoid the bands which appear in these thicknesses of *N*/1000 and more dilute solutions.

Inspection of the six curves will show that in every case the compound containing the system of four conjugated double bonds has a greater absorptive power than that which only contains three. This assumes that the benzene nucleus contains a system of three conjugated double bonds, but the conclusion is equally true if we consider the benzene system simply as a reservoir of residual affinity, for in that case we have the two unsaturated systems (nucleus and double bond) separated in eugenol and its

FIG. 2.

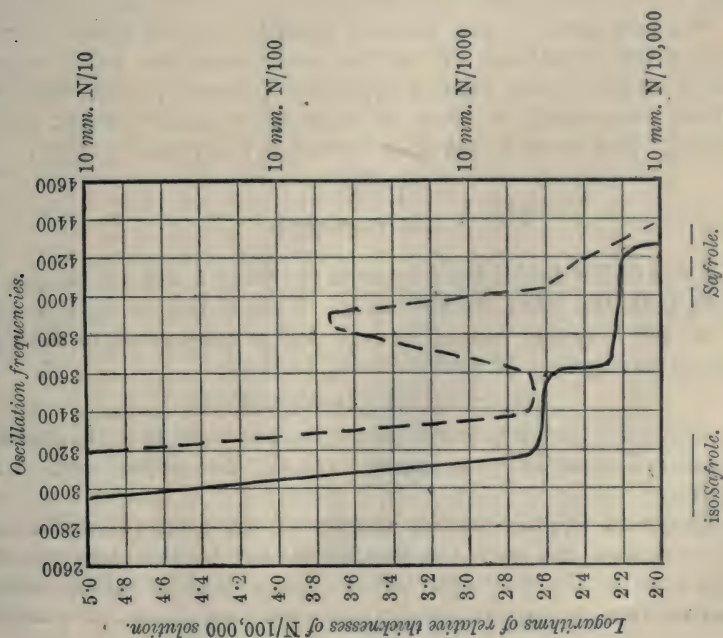
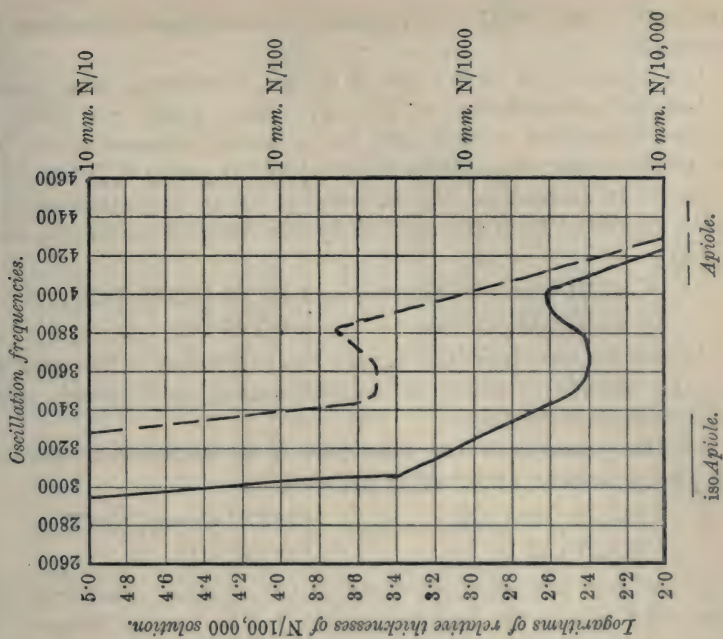


FIG. 3.



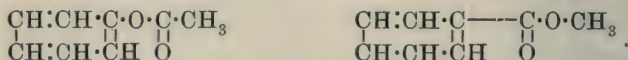
analogues, but conjugated together in *isoeugenol*, *isosafrole*, and *isoapiole*.

Let us next turn to the case of the two substances, acetophenone-oxime and acetanilide (see Fig. 4). Here again we have the benzenoid nucleus in each case, but in acetophenoneoxime we have an extra-nuclear conjugation provided by the group $\cdot\text{C}\cdot\text{NOH}\cdot$ which is absent in acetanilide, the carbonyl group in the latter substance being separated from the nucleus by the interposition of the imino-group:



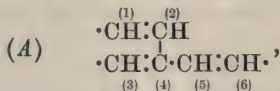
As can be seen from the curves, the rule holds in this case also, for the absorptive power of acetophenoneoxime is much greater than that of acetanilide.

Another example of the same rule is to be found in the cases of phenyl acetate and methyl benzoate:



In the first substance, we have no conjugation apart from that comprised within the benzene system, but in methyl benzoate we have the carbonyl group conjugated with the nucleus. An inspection of the curves in Fig. 5 will show that methyl benzoate has an absorptive power greater than that of the isomeric substance.

We now come to two pairs of isomerides which form a crucial test of this hypothesis. It will be remembered that in his original paper on the partial valency hypothesis (*Annalen*, 1899, **306**, 111) Thiele considered the case of what he termed "crossed double bonds," and showed that in a system of the following type:



one end of the double bond between the atoms 3 and 4 is conjugated with both the other double bonds. Now, if this be so, it is clear that such a system cannot be regarded as conjugated to the same extent as a system of double bonds, such as:



in which the partial valencies neutralise one another in the ordinary manner, leaving only one partial valency free at each end of the system.

In system (4) the partial valency of the atom (4) would have to neutralise not only the partial valency of the atom (2), but also that of the atom (5), and it is clear that in such a case as this we have incomplete conjugation. Such an instance is provided

FIG. 4.

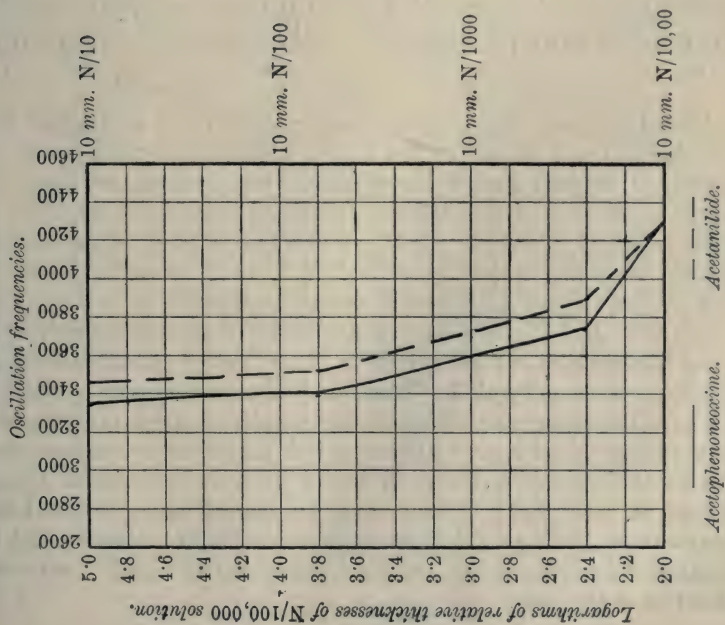
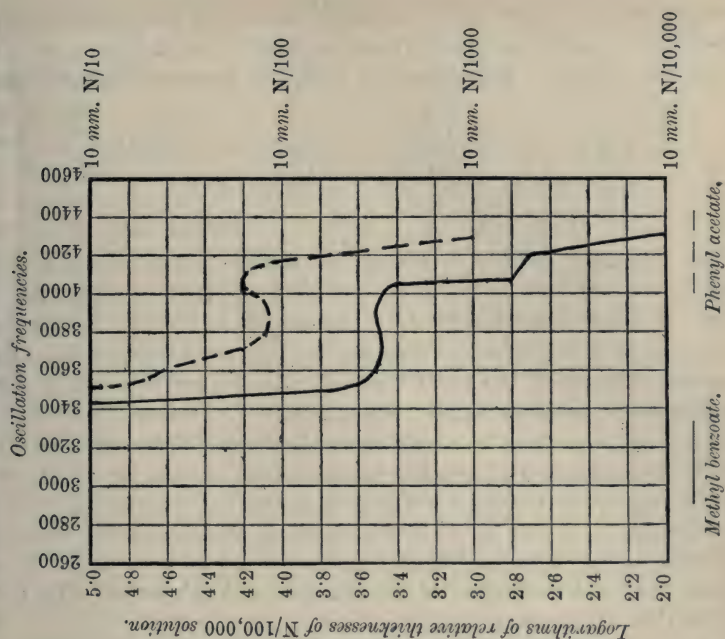
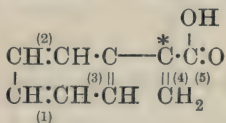


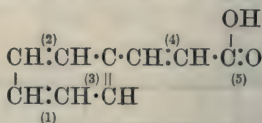
FIG. 5.



by atropic acid, for in it the double bond of the group $\cdot\text{CH}_2$ is conjugated with the double bond of the carbonyl group, and also with the nucleus. Compare this with the isomeric cinnamic acid:



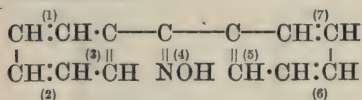
Atropic acid.



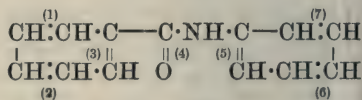
Cinnamic acid.

In cinnamic acid, the whole five double bonds form a single conjugated system, whereas in atropic acid, if we regard the first four as a conjugated system, it is clear that the fifth double bond will act as a disturbing influence, tending to absorb some of the partial valency of the atom marked with an asterisk, all of which ought to be devoted to saturating the partial valency of the atom of the benzene ring to which it is attached. It is clear therefore that in cinnamic acid we have a complete system of conjugation, including within itself all the double bonds of the molecule, whereas in atropic acid we have two conflicting systems, and we should therefore expect to find that the absorption of cinnamic acid was more powerful than that of atropic acid. A glance at Fig. 6 will show that this view is correct.

An analogous case is to be found in benzophenoneoxime and benzanilide:



Benzophenoneoxime.



Benzanilide.

Here the double bond of the group $\cdot\text{C}(\text{NOH})\cdot$ is conjugated with one double bond in each of the nuclei, whilst in benzanilide no such system of crossed double bonds exists, but, instead, we have two separate systems of conjugation. In both substances we have the same number of double bonds, namely, seven, but whilst in benzanilide we have the double bonds 1, 2, 3, and 4 forming a complete and self-contained conjugated system uninterfered with by the bonds 5, 6, and 7 of the second nucleus, in benzophenoneoxime we have the conjugated system of 1, 2, 3, and 4 disturbed by the intrusion of the bond 5. Thus, in benzophenoneoxime, although we have the same number of double bonds as in benzanilide, their distribution is such as to prevent the complete neutralisation of the partial valencies which is found in true conjugated systems except at their ends. From this, we should expect to find that benzanilide, having most true conjugation in its molecule, had the greater absorptive power, and an inspection of Fig. 7 will show that this is the case.

FIG. 6.

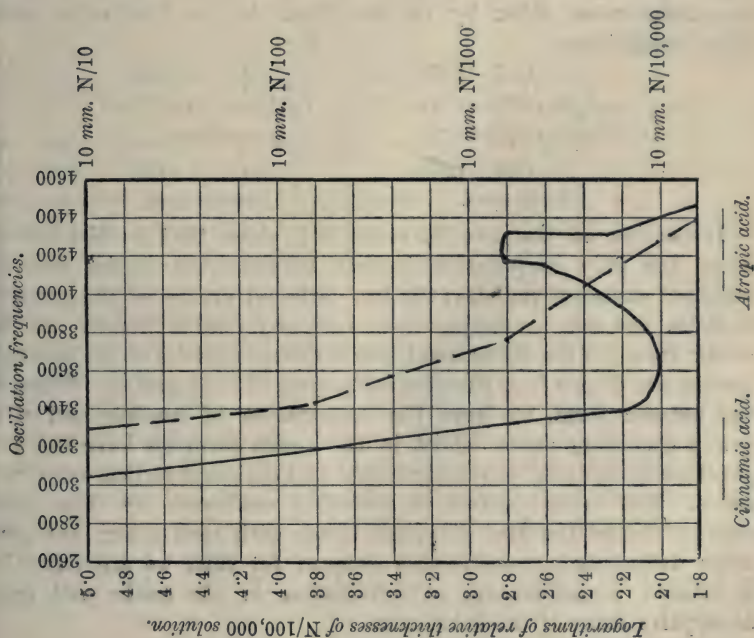
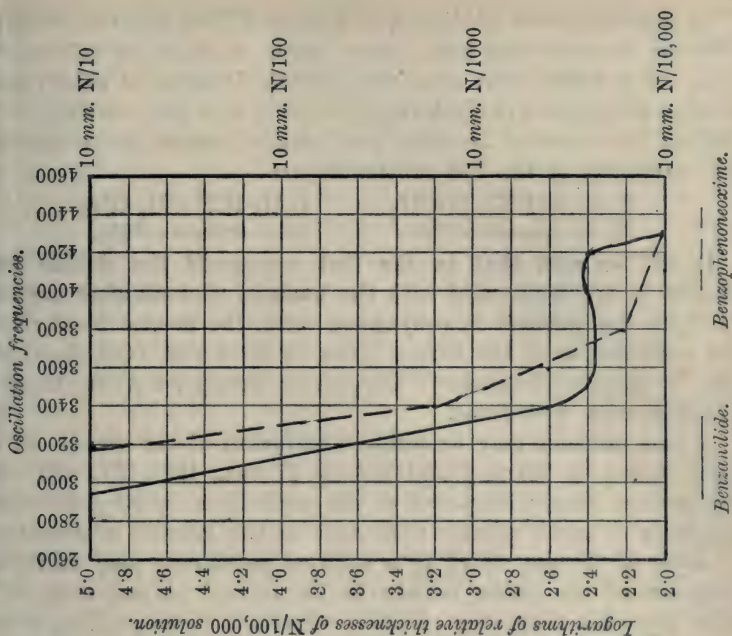
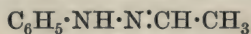


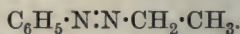
FIG. 7.



In a set of curves published by Baly and Tuck (Trans., 1906, **89**, 982) we have noticed half-a-dozen other examples of this general rule. It is known that when the phenylhydrazones of aldehydes or ketones are exposed to light, they tend to change into azo-compounds. Taking the case of acetaldehydephenylhydrazone as an example, the structures of the two substances are:



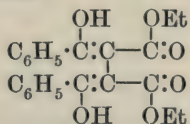
Before exposure to light.



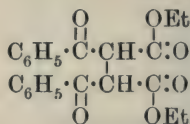
After exposure to light.

It will be seen that in the first compound the double bond $\cdot\text{N}\cdot\text{CH}\cdot$ is not conjugated with the nucleus, whereas after exposure to light the nucleus is conjugated with the double bond $\cdot\text{N}\cdot\text{N}\cdot$. An examination of the curves given by Baly and Tuck shows that the "conjugated isomeride" has greater absorptive power than the unconjugated hydrazone.

A final instance may be adduced in favour of our views. It has been shown by Hartley and Dobbie (Trans., 1900, **77**, 498) that the general absorptive power of the enolic form of ethyl dibenzoylsuccinate is much greater than that of the ketonic modifications. A layer of 25 mm. thick of a solution containing one milligram-molecule of the enolic variety in 100 c.c. of alcohol cuts off all rays beyond a frequency of 2171, whereas a corresponding experiment with the ketonic isomeride showed that light is transmitted up to a frequency of 2795. Thus the absorptive powers of the two substances differ by no less than six hundred units under these conditions:



Enolic form.



Ketonic form.

Inspection of the two formulæ will show that in the ketonic form the only conjugation is that between the nuclei and the adjacent carbonyl radicles; the two carbonyl groups of the carboxyl radicles are not in conjugation with any double bonds. In the enolic form, on the other hand, the carbonyl radicles of the carboxyl groups are drawn into the general system of conjugation. Thus, in the ketonic form, we have the conjugation of nucleus and $\cdot\text{CO}\cdot$ group occurring twice, whilst in the enolic form we have the conjugation of nucleus, ethylenic bonds and carbonyl radicle occurring twice. The latter system is probably weakened by the cross-conjugation of the two ethylenic bonds with each other, but even after deducting a considerable amount for this, we are left with a marked preponderance of conjugation in the enolic and more absorptive form of the substance.

Results similar to those which we have described above have been obtained by us in the alicyclic and open-chain compounds also, and these will furnish the basis of a future paper. The data in the present paper include fourteen pairs of isomerides of the most different types; and we believe that it is established that if we examine two isomeric substances, that which contains the greater number of true conjugated bonds within the molecule will show the greater power of general absorption. These results seem likely to be of interest in the case of terpenes containing two double bonds the relative positions of which have not been definitely established, as a comparison of their general absorptive power with that of isomeric substances of known constitution would enable us to decide whether or not the terpenes in question contained conjugated or unconjugated linkings. We might also mention that in the course of this work we have observed another relation which appears to be general. If the absorptive power of two isomeric substances, one of which is capable of conversion into the other, be examined, we have found that the stable isomeride shows greater absorptive power than the labile form, for example, *n*-propyl bromide has less absorptive power than *isopropyl* bromide, into which it can be converted by heating. This rule holds in those cases where there is no conjugated system in the molecule.

EXPERIMENTAL.

Eugenol.—This substance was obtained from Kahlbaum, and was purified by fractionation under diminished pressure.

isoEugenol.—This was obtained from Kahlbaum, and was twice distilled, the fraction boiling at 167–168° being finally taken.

Safrole.—This was obtained from Kahlbaum, and was re-distilled until it had the correct boiling point.

isoSafrole.—Obtained from Kahlbaum. On re-distillation, the middle fraction boiled absolutely constant at 251°/760 mm.

Apiole.—This was purchased from Schuchardt. It had the correct melting point.

isoApiole.—This also was obtained from Schuchardt. It was re-crystallised from aqueous alcohol until it melted at 56°.

Acetophenoneoxime.—This was prepared by one of us, and re-crystallised from light petroleum until it melted sharply at 59°.

Acetanilide.—This was a Kahlbaum specimen, purified in the usual way (m. p. 113°). Two separate specimens of the oxime and the anilide were prepared and photographed, the spectra being found to be identical.

Methyl Benzoate.—This substance was prepared by one of us by the action of benzoyl chloride on methyl alcohol. It was

fractionally distilled several times, and the fraction boiling constantly at $199^{\circ}/756$ mm. was used.

Phenyl Acetate.—This was prepared by one of us from acetyl chloride and phenol. It was purified until it boiled constantly at $195.8^{\circ}/756$ mm.

Cinnamic Acid.—Part of the curve of this substance had already been published by one of us (Stewart, Trans., 1907, **91**, 202). The compound was re-photographed at higher concentrations, and the two curves were found to be coincident.

Atropic Acid.—A specimen obtained from Schuchardt (m. p. 106.5°).

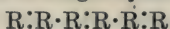
Benzophenoneoxime.—Prepared in the usual manner. Recrystallised from aqueous alcohol until it had the correct melting point.

Benzanilide.—This was obtained from Kahlbaum, and purified by recrystallisation from alcohol.

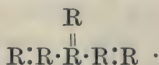
Conclusions.

1. The following rule regarding general absorption has been established. Of two isomeric substances containing two or more double bonds, the compound the molecule of which contains the longest chain of conjugations will have the greater absorptive power in the region of the spectrum above that in which any absorption bands make their appearance.

2. In the case where two isomeric substances contain the same number of double bonds, it appears that the compound containing three conjugated groups in a single system:



will have an absorptive power greater than one containing a system of so-called "crossed double bonds":



3. As this rule has been found to hold good in the case of alicyclic substances as well as in the benzene and aliphatic series, it furnishes a possibility of obtaining additional evidence of the structure of terpenes containing two double bonds the relative positions of which are not established.

In conclusion, we desire to thank the Research Fund Committee of the Society for a contribution towards the expenses of this research.

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LVI.—*The Occlusion of Hydrogen by the Palladium-Gold Alloys.*

By ARTHUR JOHN BERRY.

THE numerous investigations which have been carried out on the occlusion of hydrogen by palladium favour the view that the process consists of the solution of the gas in the metal rather than of chemical combination. Hoitsema (*Zeitsch. physikal. Chem.*, 1895, **17**, 1), in a very complete investigation of the vapour pressure of "palladium-hydrogen," concluded that two immiscible solid solutions are formed. At the same time, the precise nature of the product can scarcely be regarded as completely established.

It appeared to be of interest to investigate the absorption of hydrogen by palladium when alloyed with another metal. The palladium-gold alloys were selected for this purpose. These alloys form a complete series of mixed crystals according to Ruer (*Zeitsch. anorg. Chem.*, 1906, **51**, 391).

In a paper entitled "Additional Observations on Hydrogenium," Graham (*Proc. Roy. Soc.*, 1869, **17**, 500) described some experiments on the occlusion of hydrogen by some alloys of palladium. His results with the palladium-gold alloys in general differ very considerably from those of the present author. These results are discussed at the end of this paper.

EXPERIMENTAL.

The palladium was prepared by the reduction of the chloride by sodium formate in hot aqueous solution. After washing, the spongy metal was fused in the oxy-coal-gas flame, annealed, and rolled.

The alloys were prepared by fusing the two metals in the requisite proportions in the oxy-coal-gas flame on cupels. The buttons were then annealed and rolled, and the whole process repeated to ensure homogeneity of the product.

The occlusion experiments were conducted in the following manner. Two similar voltameters containing dilute sulphuric acid were connected together in series. The cathode of one voltameter was of the alloy the occluding power of which was under investigation. The cathode of the other voltameter, as well as the anodes of both voltameters, were of platinum. The hydrogen evolved from both cathodes was collected in measuring tubes in the usual manner. Since the same current flowed through both voltameters, the quantities of hydrogen liberated at the two cathodes were identical. The amount of hydrogen occluded by the palladium

alloy was simply measured by the difference between the two volumes of gas.

In these experiments, quantities of alloy of 0.5 to 1 gram were employed. Electrolysis was always continued for some time after the alloy appeared to be supersaturated with gas, in order to allow sufficient time for the gas to diffuse inwards. The apparatus was then allowed to stand for several hours before reading the volumes of gas. Thoma (*Zeitsch. physikal. Chem.*, 1889, **3**, 69) has shown that palladium can be supersaturated with hydrogen when charged electrolytically; the excess of gas is, however, evolved after the current ceases.

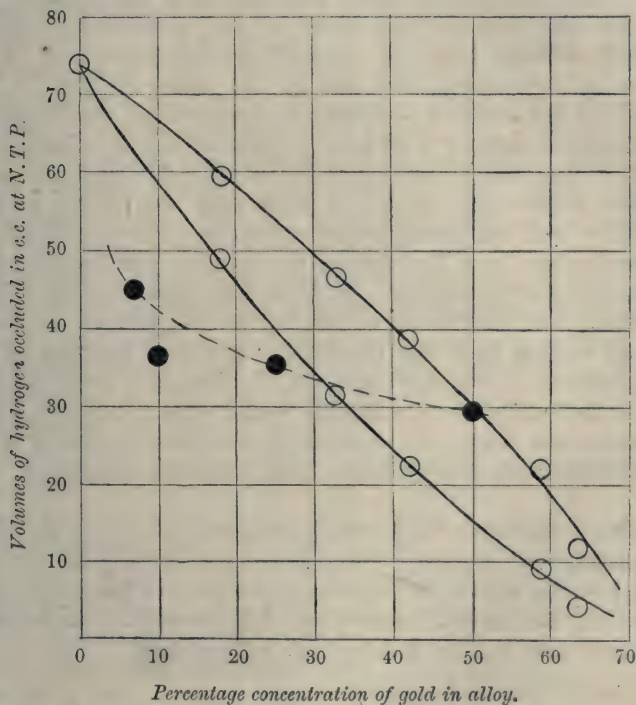
Preliminary experiments gave somewhat inconsistent results for the quantity of hydrogen occluded, and, in general, the more dilute the alloy was in respect to palladium, the greater was the difficulty in obtaining consistent results. It was subsequently found that the inconsistent results were due to incomplete annealing of the alloys before saturating them with hydrogen. Consistent results were readily obtained by annealing the alloys in an electric furnace for about two hours at a temperature of 650° before charging them with hydrogen. That the occluding power of palladium depends to some extent on the physical condition of its surface has been noted by several investigators; Mond, Ramsay, and Shields (*Phil. Trans.*, 1898, *A*, **191**, 105) have, however, shown that when the proper conditions are observed, the amount of hydrogen occluded is in all cases approximately the same.

The results are shown in the adjoining diagram. It is clear that the occluding power of alloys containing more than about 25 per cent. of palladium is a simple function of the concentration of that metal, although not simply proportional to it. For comparison, the writer has inserted the values obtained by Graham. It is clear that, with the exception of the alloy containing 75.2 per cent. of palladium, the two curves show no agreement. With regard to the alloy containing 50 per cent. of either constituent, Graham remarks as follows (*loc. cit.*): "The presence of so much gold as half its weight did not materially reduce the occluding power of palladium. Such an alloy was capable of occluding 459.9 times its volume of hydrogen with a linear expansion of 1.67 per cent." Graham does not appear to have performed any experiments with alloys more dilute in respect to palladium. For this reason, the present author is of opinion that Graham's results must not be accepted without reserve.

In order to determine whether alloys containing less than 25 per cent. of palladium were capable of occluding hydrogen, an alloy containing 19.5 per cent. of this metal and 80.5 per cent. of gold

was specially prepared. Experiments were made with 4.1745 grams of this alloy instead of with the smaller quantities hitherto employed. In no case was there any evidence of any occlusion having taken place.

The curve appears to be of the general form to be expected for the diminution of the solubility of a substance when the solvent contains increasing quantities of an inert diluent. The question as to why occlusion should cease altogether when the concentration



Upper curve : Occlusion per gram of palladium.

Lower " : " " " alloy.

Broken curve and black points : Graham's results per gram of alloy.

of the palladium falls below about 25 per cent. does not appear to be obvious. It would be premature to attempt to frame any hypothesis to explain this phenomenon at present. It is intended to investigate the occluding properties of other alloys of palladium, and it is hoped that some light may be thrown on the matter.

Before concluding this paper, the writer desires to call attention to some experiments performed by Shields (*Proc. Roy. Soc. Edin.*, 1898, **22**, 169) on the electromotive force of the combination:

palladium containing much hydrogen, dilute sulphuric acid, palladium containing little hydrogen. Shields calculated the electromotive force of such a cell from the well-known equation:

$$E = \frac{RT}{ne} \log_e \frac{p}{p'}$$

Experiment, however, showed that the electromotive force of the system approximated to zero, and Shields concluded that since the system apparently did not behave as a true concentration cell, a definite compound of palladium and hydrogen was formed. In calculating the electromotive force of the combination, Shields apparently assumes that the ratio of the concentrations of the hydrogen in the concentrated and in the dilute solutions is proportional to the ratio of the osmotic pressures of the hydrogen. This assumption appears to be quite unjustifiable, and, indeed, there is definite experimental evidence against it. An examination of Hoitsema's curves (*loc. cit.*) will show that the vapour-pressure curve at the ordinary temperature continues almost horizontal to the concentration axis throughout the greater part of its range, after which it rises rapidly. It is almost certain that Shields' experiments were performed on the horizontal part of the curve, and if we assume that the vapour pressure is a measure of the osmotic pressure of the hydrogen, an electromotive force approximating to zero is precisely what one would expect. Consequently, this phenomenon cannot be regarded as evidence in favour of the view that palladium and hydrogen form a definite compound.

The author desires to express his sincere thanks to Professor Pope for suggesting the subject of this investigation to him, and for allowing him the use of the palladium chloride for the preparation of the alloys, and to Mr. Heycock for the interest he has taken in these experiments and for his valuable suggestions.

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LVII.—*The Determination of the Dissociation Pressures of Hydrated Salts by a Dynamical Method.*

By JAMES RIDDICK PARTINGTON.

PROBABLY no branch of physico-chemical investigation has aroused a more lively and sustained interest than that dealing with the dehydration of the so-called molecular compounds of water with substances which are electrolytically dissociated in aqueous solution

—the hydrated salts. The study of this phenomenon by the measurement of the pressure of water vapour in contact with the partly dehydrated salt has claimed the attention of many investigators, and a rich store of numerical data has been amassed. The experimental methods employed may be classified into:

(1) *Statical Methods*, depending on a determination of the pressure of water vapour which has been kept in contact with partly dehydrated salt for a comparatively long time, and including the *Tensimetric Method*, introduced by Mitscherlich, in which the pressure is recorded directly by a gauge, and the *Dew-point Method* of Lesœur, in which the pressure is determined by the temperature of a surface on which the vapour deposits dew.

The fact, first asserted by Wiedemann (1866), that such a pressure is definite for a given pair of solid phases, and is a function of the temperature alone, may be regarded as established, although some earlier workers (Precht and Kraut, *Annalen*, 1875, **178**, 129; A. Naumann, *Ber.*, 1874, **7**, 1573) were inclined to believe that they had evidence that this was not the case.

(2) *Dynamical Methods*, of which three types have been utilised:

(i) *The Diffusion Method*, of Müller-Erzbach, in which the vapour formed from the hydrate at the bottom of a cylindrical tube is allowed to diffuse up and out of the tube. The loss in weight after a given time, and the loss in weight of a similar tube containing water, provide the data required.

(ii) *The Transpiration Method*, in which the water removed from the hydrate by a slow stream of air is determined. From this, the vapour pressure may be calculated, on the assumption that water vapour under this pressure obeys the gas laws, either by measuring the volume of air aspirated, or by comparing the weight of water vapour carried away from the hydrate with that carried off from pure water by the same volume of air.

(iii) *Linebarger's Method*, depending on the change of boiling point of a solvent which dissolves water only sparingly, by the introduction of hydrated salt.

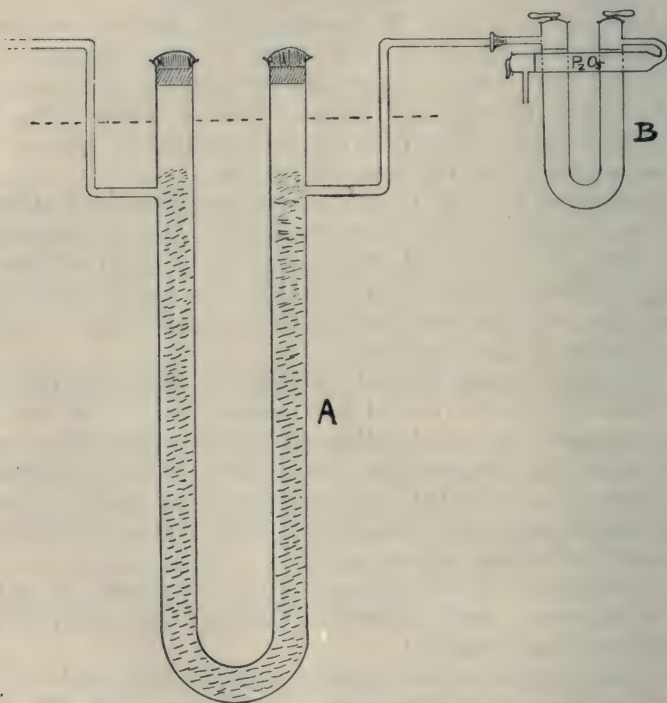
The transpiration method appears to have been used in one research only, namely, by Tammann (*Wied. Ann.*, 1888, **33**, 329), who measured the volume of air passed over the hydrate. He observed that dissociation pressures measured in this way are appreciably higher than those determined tensimetrically. The difference he explained as due to the presence of traces of saturated solution retained by the crystals. H. Schottky (*Zeitsch. physikal. Chem.*, 1908, **64**, 433) has carried out a series of tensimetric measurements with great care, and has observed a similar abnormally high pressure during the initial stages of a static measurement.

He adopted Tammann's explanation: "Schwer zu vermeiden war ferner eine Störung, die wohl der Adsorption, dem Festhalten einer Lösungshaut an den grossen Oberflächen der gepulverten Salze, zuzuschreiben ist. Nach frischer Beschickung des Apparates traten zunächst viel zu grosse Drucke auf."

EXPERIMENTAL.

The author has carried out a number of experiments by the transpiration method, but instead of measuring the volume of air

FIG. 1.



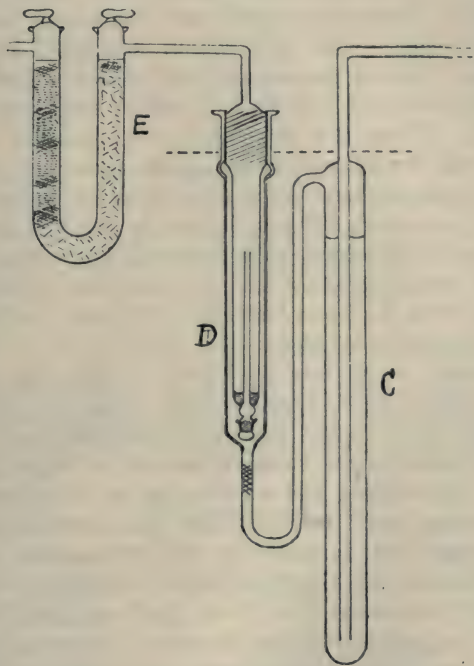
aspirated through the apparatus, which involves troublesome corrections for changes of barometric pressure, the air, after passing over the hydrate, was allowed to bubble through water at the same temperature. If w_1 , w_2 are the weights of water removed from the hydrate and pure water respectively, at any temperature θ , it is easily shown that:

$$p\theta = \frac{w_1}{w_2} \pi\theta \dots \dots \dots (1).$$

where p_θ , π_θ are the dissociation pressure of the hydrate and the vapour pressure of water respectively, with the same assumption as before.

Two forms of apparatus were used, the first (Figs. 1 and 2) for low temperatures (20° , 25°). The hydrate was contained in the U-tube *A*, which was 30 cm. in height and 2 cm. in diameter. This was closed by well-paraffined corks covered outside with soft wax, and was connected on one side with a series of drying towers and a small gas meter, on the other with an absorption tube *B*,

FIG. 2.



containing calcium chloride and phosphoric oxide. Ground-glass joints, covered with a thin layer of vaseline, were used for connecting all parts of this and the second apparatus, in which water vapour was present. Rubber connexions and stoppers are quite useless in such cases, on account of their hygroscopic nature. The tube *B* was connected through a protective drying tube by a piece of lead tubing and rubber pressure-tubing joints with the water-bubbler *C*, a plain glass washing-tube, 20 cm. long and 2 cm. in diameter, which communicated with a trap *D*, in which fitted, by a ground joint, the absorption tube *E*, containing calcium chloride

and phosphoric oxide. A little glass wool was placed in the tube between *C* and *D*. The tube *E* was connected, through a small wash-bottle containing frequently renewed concentrated sulphuric acid, with two large empty bottles with regulating taps, and these, finally, were attached to a water-pump.

The absorption tube *E*, closed below with a ground cap, was placed in the trap *D* for about five minutes before the commencement of every experiment, so as to assume the temperature of the thermostat, in which the whole was immersed up to the dotted line.

The volume of air aspirated varied from three to six litres according to the temperature, and each aspiration occupied from four to twelve hours. The air bubbled through *C* at the rate of about two small bubbles per second, and always passed through at a perfectly uniform rate, although *A* was in some cases filled with powdered salt. When the experiment was finished, all the taps were closed, and the absorption apparatus detached, cleaned from lubricant by means of benzene, and weighed by Borda's method.

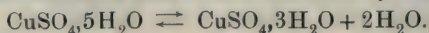
The second apparatus differed only from the first in having the *U*-tube, the ends of which were hermetically sealed, completely immersed, and communicating with an absorption apparatus exactly like that used with the water-bubbler. All danger of condensation on cool parts was thus avoided.

The thermostat, which was fitted with a plate glass window, was stirred by a small paddle placed to one side, and mounted on a shaft working in a bicycle hub with ball-bearings. This, when driven by an electromotor, threw a current of water upwards, and at the same time caused the whole mass to circulate. This is a method of stirring much more efficient than that in which a large paddle, covering the bottom of the thermostat, is used. A Beckmann thermometer, compared with a standard, was used, and the bath could, by means of a Lowry bulb-regulator, be kept at a temperature varying by 0.005° at the most, for several days, without attention. At the higher temperatures the water was covered with a layer of cylinder oil.

Most of the water condensed in the upper part of the tube leading from the trap, and was retained by an obvious device shown in the diagram.

A. Copper Sulphate Hydrate.

The first measurements were made with the system:



Purified and recrystallised copper sulphate was used; the specimen prepared was in very small crystals, which were kept for six hours

in a press between filter paper, and then air-dried for a week. A column of 10 cm. was put in the U-tube, air aspirated through for about six hours, and the measurements begun. After the experiments, the salt was seen to have effloresced for a depth of 0.5 cm. next the air-inlet, this part being separated sharply from the rest, which was apparently unchanged.

Temperature = 25.01° . $\pi_{25.01} = 23.560$ mm.

w_1 .	w_2 .	$p_{25.01}$ mm.
0.0075	0.0232	7.61
0.0085	0.0245	8.13*
0.0066	0.0186	8.36*
0.0065	0.0203	7.54
0.0176	0.0519	7.98
0.01924	0.0594	7.28
0.01157	0.03610	7.55
0.00949	0.02776	8.05
0.00744	0.02263	7.74

The mean (rejecting those numbers marked *) is $p_{25.01} = 7.68$ mm.

The value interpolated from Frowein's tensimetric results (*Zeitsch. physikal. Chem.*, 1887, 1, 5) is $p_{25.01} = 7.35$ mm.

The dynamic pressure is thus slightly higher than the static pressure.

B. Barium Chloride Hydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

For various reasons, it appeared desirable to use a hydrate containing less water than copper sulphate pentahydrate, and barium chloride dihydrate was next taken, purified by recrystallisation.

Temperature 25.01° .

w_1 .	w_2 .	$p_{25.01}$ mm.
0.00690	0.03112	5.20
0.01013	0.04503	5.30
0.01390	0.04728	6.92*
0.01152	0.03766	7.20*
[25.03°] 0.01138	0.04222	6.34*
0.01064	0.04576	5.26
0.01108	0.04952	5.27

The mean value adopted is $p_{25.01} = 5.26$ mm. Frowein's interpolated value is 5.20 mm.

Some irregularities were observed with this substance, and the experiments were not extended to higher temperatures.

C. Racemic Acid Hydrate, $(\text{C}_4\text{H}_6\text{O}_6 \cdot \text{H}_2\text{O})_2$.

Kahlbaum's "pure racemic acid" was used; 100 grams were reduced to a coarse powder and placed directly into the U-tube.

(a) Temperature $25\cdot00^{\circ}$. $\pi_{25}=23\cdot546$ mm.

(a)	w_1 .	w_2 .	p_{25} mm.
	0·00454	0·03854	2·77*
	0·00840	0·04251	4·66*
	0·01069	0·04591	5·49*
	0·01672	0·03994	9·85
	0·02660	0·05550	11·29
	0·01701	0·04415	9·08
	0·02044	0·04934	9·65
	0·02196	0·04890	10·58
	0·01943	0·04293	10·66
	0·03004	0·06889	10·27
	0·01571	0·03377	10·96
	0·01409	0·03299	10·08

The mean result is $p_{25}=10\cdot37$ mm.

(β) The acid, which had effloresced only near the inlet tube, was removed, well mixed, and replaced. The following numbers were obtained:

0·01095	0·03186	8·104*
0·01595	0·03667	10·24
0·01617	0·03776	10·35

(γ) The acid was now removed, mixed, and distributed in three horizontal U-tubes. A current of dry air was passed over for four hours, the solid being frequently shaken so as to expose new surfaces. The whole was well mixed and recharged into the experimental tube. The results were:

0·01977	0·04416	10·51
0·01810	0·04185	10·19

(δ) The acid was removed, spread out on a large porous plate, and placed in a vacuum desiccator over calcium chloride for an hour. After mixing, it was replaced by the experimental tube:

	0·01090	0·02216	11·59*
	0·03096	0·04623	15·77*
[24·99°]	0·02142	0·05141	9·805*
	0·01838	0·04104	10·55

The mean result from (α) to (δ) adopted is $p_{25}=10\cdot33$ mm.(b) Temperature $20\cdot27^{\circ}$. $\pi_{20\cdot27}=17\cdot696$ mm.

	w_1 .	w_2 .	$p_{20\cdot27}$ mm.
	0·00655	0·02488	4·66*
[20·29°]	0·00958	0·03326	5·96
	0·01008	0·03701	4·82*
[20·295°]	0·01112	0·03493	5·62*
	0·01447	0·03763	6·81
	0·02270	0·04992	8·05*
	0·01766	0·05422	5·81

Mean result adopted is $p_{20\cdot27}=5\cdot61$ mm.

(c) Temperature 29.89° . $\pi_{29.89} = 31.384$ mm.

w_1 .	w_2 .	$p_{29.89}$ mm.
0.01799	0.03823	14.77
0.02615	0.04761	17.16
0.01923	0.03201	18.85
0.02795	0.04620	18.98
0.03107	0.05636	17.30
0.02040	0.03423	18.70

Mean result adopted is $p_{29.89} = 18.19$ mm.(d) Temperature 40.00° . $\pi_{40} = 54.97$ mm.

w_1 .	w_2 .	p_{40} mm.
0.06570	0.08408	42.96
0.05295	0.06951	41.87
[40.04°] 0.04299	0.05268	44.86
0.05505	0.07144	42.36
0.04385	0.05577	43.22

Mean: $p_{40} = 43.05$ mm.(e) Temperature 50.00° . $\pi_{50} = 92.17$ mm.

w_1 .	w_2 .	p_{50} mm.
0.09297	0.10784	79.49
0.08559	0.09542	82.66
0.16325	0.18573	81.02
0.08464	0.09667	80.69

Mean: $p_{50} = 80.96$ mm.*Discussion of the Results.*

The numbers for racemic acid hydrate have been represented graphically in Fig. 3. The perfect regularity of the curve shows that the pressure measured by the transpiration method is a definite magnitude, whatever interpretation may be put upon it.

The mean pressures of series (A) and (B) confirm Tammann's statement as to the higher value of the dynamic as compared with the static pressure,* but it is believed that the results of series (C) entirely exclude any possibility of explanation by the supposed presence of saturated solution, and are in agreement with the theory indicated by the author in a previous communication (Proc., 1911, 27, 12).

There are three possible explanations of the higher values of the dynamic pressure:

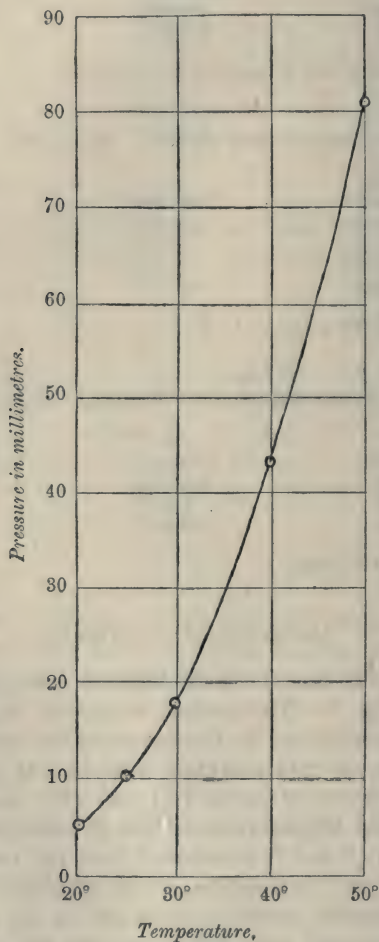
(1) That they are a consequence of incorrectness of the assump-

* Some further experiments with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ indicate that the pressure at 25° is probably rather higher than the one recorded; the value 5.50 seems to be probable.

tion that water vapour at the pressures considered obeys the gas laws.

This explanation is excluded by Schottky's observation that the phenomenon also appears in the initial stages of a tensimetric measurement.

FIG. 3.



(2) That they are due to the presence of saturated solution retained on the crystals, or occluded in their interior.

The solution could scarcely have been occluded in the interior of the very small crystals of copper sulphate used in the experiments now described, and, if present at all, must have been adherent to the surface. If this were the case, the pressures recorded in

the first one or two experiments should always be higher than those in the later ones. Exactly the reverse is observed; the initial pressures are either very small, the pressure then rising steadily as the extent of dehydration proceeds, and finally attaining a steady value which is higher than the tensimetric pressure, or else steady all through the series. The first phenomenon is observed with series $C(a), [\alpha]$, $C(a), [\beta]$, $C(c)$, especially in the first, where no previous dehydration had occurred; the second is characteristic of series (A) and (B), in which the salt was dehydrated to a fairly considerable extent before beginning the measurements.

This fact, taken in connexion with another to be mentioned immediately, leaves open only the third hypothesis:

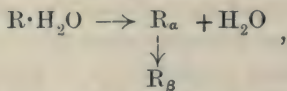
(3) That the phenomena are simply and completely explained by the initial production of an unstable, probably amorphous, lower hydrate or anhydrous salt, which passes slowly into a stable, crystalline modification.

The initial formation of such a substance is rendered probable, from an inductive point of view, by Ostwald's Principle of Successive Reactions, and is apparently also in agreement with the representation of the process of dehydration which is given by the molecular theory. The vapour pressure of a pure liquid is the same whether determined statically or dynamically. The necessary conditions for this are obviously that the surface of separation of the two phases remains unaltered in character when either phase is increased at the expense of the other, and that the readjustment of temperature in the liquid can, by conduction of heat to it from the surroundings, occur sufficiently rapidly. In the case of a pair of isotropic phases (for example, pure liquid and vapour), these can be fulfilled, because the equilibrium is attained and maintained by the statistical equality in the numbers of molecules leaping out of, and returning to, the liquid in any interval of time. By reason of the wholly unco-ordinated molecular motion in each phase, the transference of a finite amount of one phase to the other can produce no effect on the losing phase, which could not have been produced by withdrawing a portion of the phase in bulk, which, of course, has no influence on the equilibrium. If, however, one of the phases is a crystalline solid, this is not necessarily the case. In a crystal of a hydrated salt, one may suppose that the molecular aggregates of anhydrous salt and attached water are oscillating in small excursions about fixed points which are arranged in definite space-lattices ("Raumgittern"), determining the crystalline form. If the kinetic energy of one of these aggregates exceeds a certain finite amount, the component molecules part company, and the molecules of water are ejected forcibly from the space-lattice. This

will produce a disruption of that portion of the lattice adjacent to the centre of disturbance; it breaks down, and the molecules of solid lower hydrate, or anhydrous salt, remaining behind fall together into an amorphous aggregate which only slowly rearranges itself into a new space-lattice, and so gives rise to a stable, crystalline form. The molecules of water, which now form an isotropic vapour phase, can obviously not return to their original positions in the first space-lattice, and a condition of mobile equilibrium, exactly analogous to that existing between a liquid and its vapour, is excluded by the nature of the system (compare Schenck, *Centr. Min.*, 1900, p. 313, who finds that the dissociation pressure is different over different crystal-faces).

The molecular theory of dehydration of a crystalline hydrate has, along with other dissociation phenomena in heterogeneous systems of similar character, offered difficulties which do not appear to be completely overcome even at present. The case under discussion may, however, be considered from another point of view, which, whilst it does not enable us to see all that is going on during the process, is at least in agreement with the observed phenomena.

If we regard racemic acid hydrate for simplicity as $C_4H_6O_6 \cdot H_2O$, or $R \cdot H_2O$, we can represent the process of dehydration as follows:



in which R_α is the unstable form first produced, which passes slowly into the stable, crystalline form, R_β .

The dissociation pressure of water vapour over such a system will be a function, not only of the temperature, but also of the absolute and relative amounts of R_α , R_β present; it will, for example, be zero over a perfectly uneffloresced crystal, when:

$$R_\alpha = R_\beta = 0.$$

The removal of water doubtless occurs at a definite number of centres of efflorescence which are distributed throughout the salt. These spread through the mass, and a limited region of efflorescence is formed in the vicinity of the air inlet-tube. The extent of this region will depend on the facility with which dehydration occurs, and on the number of pre-formed nuclei. It was found, for example, that a much longer column of barium chloride hydrate was required to attain saturation than of copper sulphate hydrate, although the dissociation pressures are not greatly different. The initial period of small vapour pressure therefore corresponds with the formation of an efflorescence region. When such a region is formed, the process of dehydration is confined to that part of the

system. Now the first product of dehydration will be the unstable lower hydrate, and when sufficient of this has accumulated, the pressure attains saturation. All the time, however, this hydrate is passing over into its stable crystalline form, in contact with which the vapour exists at a smaller pressure. There will obviously be a time when the amounts of R_α and R_β are so adjusted that the pressure attains a maximum. Further dehydration leads to a falling, but ultimately steady, pressure, because the latter is now determined principally by the large surface of R_β , in comparison with which the newly-formed R_α is negligible. The presence of the R_α shows itself, however, in the somewhat larger value of the steady dynamic pressure as compared with the static or tensimetric pressure, where the system has been left for a time which allows the whole of the R_α to pass into stable R_β .

The strict mathematical treatment of the system, which resembles that of motion in some dynamical systems, is without interest in this case, on account of the complications introduced by the experimental method; the results could show nothing beyond what has just been stated, and the discussion is omitted here. It may be observed, however, that a treatment of somewhat simpler systems than the present, such as occur, for example, in the "ageing" of deposited catalytic surfaces, would present points of interest, and this will probably form the subject of a later communication.

Measurements of the tensimetric pressure of racemic acid hydrate, and of some thermal magnitudes, are also in progress, with a view to comparison of the results with Nernst's new theory.

Summary.

(1) A method of measuring the pressure of water vapour in contact with a salt hydrate has been elaborated. The weight of water lost by the hydrate in a current of air is compared with that lost by pure water, in a special apparatus.

(2) The results with copper sulphate pentahydrate, barium chloride dihydrate, and racemic acid hydrate show that the initial pressures are very small, but with increasing dehydration the pressure rises, attains a maximum, and then falls to a steady value which is slightly higher than the value obtained by tensimetric (static) methods.

(3) These results are shown to be in accordance with the view that the first product of dehydration is an unstable, probably amorphous, lower hydrate or anhydrous salt, which slowly passes into a stable, crystalline form. They exclude the explanation suggested by Tammann that the somewhat higher value of the

dynamic pressure is due to saturated solution adsorbed on the solid salt.

In conclusion, I desire to thank Dr. Lapworth for the interest he has shown during the course of the work.

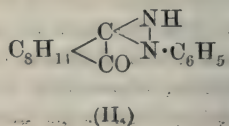
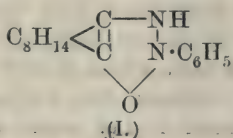
CHEMICAL DEPARTMENT,
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LVIII.—*Studies in the Camphane Series. Part XXIX.* *A New Phenylhydrazone of Camphorquinone.*

By MARTIN ONSLOW FORSTER and ADOLF ZIMMERLI.

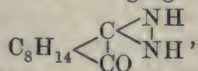
CAMPHORQUINONEPHENYLHYDRAZONE was first described by Claisen and Bishop (*Sitzungsber. K. Bayer. Akad.*, 1890, 460, 478). They prepared it from hydroxymethylenecamphor and benzenediazonium chloride, whilst Claisen and Manasse (*Annalen*, 1893, **274**, 87) utilised it in their characterisation of camphorquinone, which they subjected to condensation with phenylhydrazine. Betti (*Ber.*, 1899, **32**, 1995), who produced it by the action of benzenediazonium chloride on sodium camphorcarboxylate, claimed to recognise an enolic form of the substance, answering to the ferric chloride test and melting at 180°, in addition to a ketonic form which melted at 155° and did not develop colour with ferric chloride, whilst a third material, giving colour with ferric chloride, melted at 165°, and was regarded by Betti as a "keto-enolmisch-form." Lapworth and Hann, who were the first to draw attention to the mutarotation displayed by solutions of the phenylhydrazone (*Trans.*, 1902, **81**, 1514), threw doubt on the separate existence of any but the substance of highest melting point, agreeing, however, with Betti's conclusion that it probably represents the pure enolic form, $C_8H_{14} \begin{smallmatrix} \diagup C \cdot N : N \cdot C_6H_5 \\ | \\ C \cdot OH \end{smallmatrix}$, which undergoes incomplete trans-

formation into a ketonic modification when dissolved, as indicated by the alteration in optical activity. These views were not accepted by Armstrong and Robertson (*Trans.*, 1905, **87**, 1272), who suggested that the derivative of high melting point is to be represented by the formula (I), and that on dissolution in benzene



it is changed, to the extent of about 10 per cent., into the isomeric substance (II). The last-named investigators, however, did not adduce any chemical evidence for their conclusions, which were based on convictions as to relation between structure and such optical properties as colour and rotatory power. Two years later, Baly, Tuck, Marsden, and Gazdar were led from a study of absorption spectra to regard the phenylhydrazone and *p*-bromophenylhydrazone of camphorquinone as having the conventional ketonic formula in neutral solutions, recognising a modification of this structure in presence of sodium ethoxide (Trans., 1907, **91**, 1572); they were not able to find any spectrochemical support for difference in type of structure between the diphenylhydrazone and other condensation products of camphorquinone, such as Armstrong and Robertson believed they had brought to light. A few months ago Auwers recorded attempts to recognise an isomeric form of the phenylhydrazone; these led consistently to the isolation of one modification only, "die alle Kennzeichen einer einheitlichen Substanz aufwies" (*Annalen*, 1910, **378**, 245), and regarded by the author as a conventional phenylhydrazone.

We have recently described experiments dealing with the action of hydrazine, semicarbazide, and phenylcarbamyldrazide on camphorquinone, which, in our opinion, point to the existence of stereoisomerism among the products, similar in nature to that prevailing among oximes as represented by the Hantzsch-Werner hypothesis (Trans., 1910, **97**, 2156). The conclusion was based on the discovery of two isomeric hydrazones, which were not only directly convertible into diazocamphor by oxidation, but which also arose from that substance by mild reduction. The absence of any grounds, stereochemical or otherwise, for representing the hydrazine residue in these derivatives as belonging to the cyclic type:



seemed to point unmistakably to stereoisomerism of the above-mentioned character, and to stamp these isomeric substances as conventional hydrazones with azethenoid linking. In these circumstances, it appeared to us possible that a more careful search for the missing phenylhydrazone would bring this substance to light, and would show that it is allied to the existing compound by a relationship similar to that which connects the two hydrazones. This inquiry has resulted in the isolation of such an isomeride, which we propose to call the β -phenylhydrazone, referring to the better known derivative as the α -phenylhydrazone.

Camphorquinone- β -phenylhydrazone is a bright yellow, crystalline substance, melting at 36° , and having $[\alpha]_D$ 375° in an alcoholic solu-

tion of 1 per cent. It is very much more freely soluble than the α -modification, and is slightly volatile in steam. It is produced in association with the less fusible compound when camphorquinone undergoes condensation with phenylhydrazine, but as the equilibrium is being continually disturbed by the separation of sparingly soluble solid, the proportion obtained in this way is very small. A more convenient source is the α -phenylhydrazone itself, which yields about 90 per cent. when the temperature of the fused substance is raised to 210° , the β -phenylhydrazone being separated from the resulting mixture by distillation in steam or by extraction with a small proportion of cold petroleum. When heated, either alone or in alcoholic solution, it is transformed into an equilibrium mixture with the α -modification; by following this change in the polarimeter, it is possible to show that the same proportion of the two isomerides constitutes this mixture, whether the material originally dissolved is the α - or the β -modification.

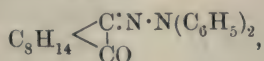
Thus, in all respects, the new phenylhydrazone fits into the gap in the series of condensation products from camphorquinone and hydrazine, semicarbazide, phenylcarbamyldiazide, and phenylhydrazine, as shown in the following table:

Derivative.	α -Series.		β -Series.	
	M. p.	$[\alpha]_D$.	M. p.	$[\alpha]_D$.
Hydrazone.....	206°	287°	102°	231°
Acetylhydrazone	239	265	150	224
Semicarbazone	236	278	147	201
Phenylcarbamyldiazide	211	229	161	192
Phenylhydrazone	190	431	36	375

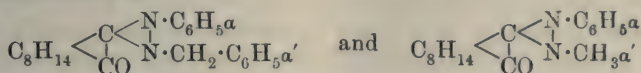
The regularity in declension of melting point and specific rotatory power on passing from the α - to the β -series is so marked as to suggest that the relationship which connects the members of a pair is the same in each case, and thus the argument for regarding the two phenylhydrazones as stereoisomeric seems a strong one, provided this view of the hydrazones themselves can be accepted. There is one point, however, in which the phenylhydrazones differ from their prototypes. Whilst these of the α -series are colourless in distinction from the pale yellow colour of their β -modifications, the α -phenylhydrazone has approximately the same tint as the β -hydrazone, and the β -phenylhydrazone is bright yellow. We are aware that Armstrong and Robertson believe the α -phenylhydrazone to be colourless, but they are the only chemists who have made this claim, and it is by no means clear that they ever produced it in this condition, the nearest recorded approach being a specimen described by Robertson (Trans., 1905, **87**, 1298) as "all but white" under benzene, becoming "very pale yellow" on drying. It does not seem to us improbable, however, that the α -phenylhydrazone

should be faintly coloured, even though the parent hydrazone is colourless, as the effect might be reasonably expected from the phenyl group, which undoubtedly exerts an auxochromic influence when replacing hydrogen in the β -hydrazone.

To the arguments brought against possible differences in structure between members of the two series, we have nothing to add to our previous communication, excepting that there is not the slightest ground for regarding the β -phenylhydrazone as an enolic form of the less soluble modification; moreover, this opening seems to have been effectually closed by Baly, Tuck, Marsden, and Gazdar. Furthermore, it is no longer proper to speak of stable and labile forms of camphorquinonephenylhydrazone; both are stable in the solid phase, both are labile when dissolved. It is necessary, also, to correct a misconception as to the mutarotation of the α -phenylhydrazone in alcohol, which Lapworth and Hann regarded as taking place so rapidly that the specific rotatory power reaches its final value before an observation can be made. As a consequence of our experiments, it appears more probable that at this stage the mutarotation has not begun, because the rotatory power is rapidly diminished on heating, and arrives finally at a point approximately the same as that to which the rotatory power of the β -phenylhydrazone may be raised by similar treatment. Another misunderstanding, embodied in Robertson's conclusion that "the labile form has practically no rotatory power," is also removed, and carries with it whatever support that deduction may be regarded as giving to the views of Armstrong and Robertson concerning the constitution of the condensation products of camphorquinone. It appears to us, in fact, that the whole case for regarding camphorquinonephenylhydrazone as structurally abnormal is undermined. The basis of the argument was the low molecular rotatory power (420°) of the diphenylhydrazone,



when compared with those (2200° and 2430°) of the phenylbenzylhydrazone and phenylmethylhydrazone, represented by Armstrong and Robertson as:



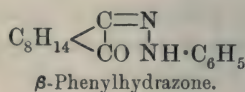
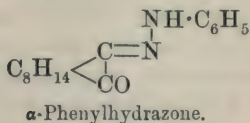
respectively, coupled with the deep yellow colour of the first-named substance as compared with the "colourless" and "almost colourless" appearance of the others. The intermediate molecular rotatory power (850°) of the phenylhydrazone, which they also describe as colourless, led them to represent it by a third type of

formula, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{N} \cdot \text{C}_6\text{H}_5 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$, and believing that in benzene

solution about one-tenth of this substance is converted into "a metameride having little, if any, optical activity," they regard this hypothetical product as being similar in type to the phenylbenzylhydrazone and phenylmethylhydrazone, but in order to explain the supposed absence of optical activity, they place the

phenyl group in the alternative position, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \text{---} \text{NH}\alpha \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{N} \cdot \text{C}_6\text{H}_5\alpha' \end{array}$.

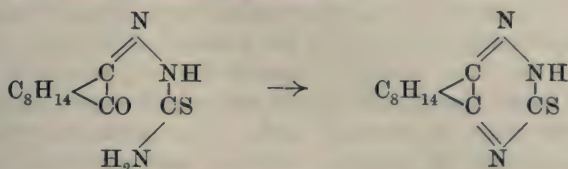
It is difficult to take these speculations seriously, since not one shred of chemical evidence has been brought forward in support of them, and they appear to us especially untrustworthy now that the substance which Armstrong and Robertson, without having isolated it, described as colourless and inactive, proves, when isolated, to be bright yellow and possessed of specific molecular rotation 948° in benzene solution. The scheme adopted in dealing with the hydrazones, semicarbazones, and phenylcarbamyldiazones, on the other hand, would classify the α - and β -phenylhydrazones as *anti*- and *syn*-carbonylic respectively:



and the comparatively strong colour of the β -phenylhydrazone would then find its explanation in the concentration of unsaturated atoms prevailing in the *syn*-configuration.

Concurrently with these experiments, we have studied the thiosemicarbazone and phenylthiocarbamyldiazone of camphorquinone, and find that it is not possible in either case to isolate more than one modification. When condensation takes place between the diketone and thiosemicarbazide, the α - and β -modifications are certainly produced, but the facility with which the latter is transformed into the thiotriazine by loss of water precludes its isolation; thus the case of the thiosemicarbazones resembles that of the benzilsemicarbazones, of which one modification only is known, the substance supposed originally to be the isomeride having been shown by Biltz and Arnd (*Ber.*, 1902, **35**, 344) to consist of the diphenyloxytriazine. The properties of the α -thiosemicarbazone, which dissolves in alkali without undergoing change, agree with what might be expected from the replacement of oxygen by sulphur in the α -semicarbazone.

As regards the thiotriazine produced by the intramolecular condensation of the β -thiosemicarbazone,

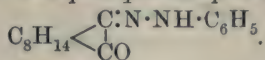


there is reason to believe that the foregoing representation is less applicable to the sulphur compound than is the corresponding formula to the oxytriazine. The behaviour of the silver salt, which loses silver sulphide by the action of boiling water, seems to indicate the alternative expression for the thiotriazine, that, namely, containing the $\text{N}:\text{C}\cdot\text{SH}$ group. Some difference in type of structure between the oxytriazine and the thiotriazine would appear also to be indicated by the fact that, whilst the exchange of oxygen for sulphur in the semicarbazone and phenylcarbamyldihydrazone is attended with elevation of specific rotatory power, amounting to 38° and 30° respectively, the thiotriazine has $[\alpha]_D -73.3^\circ$, as compared with $[\alpha]_D 22.6^\circ$ observed for the oxytriazine.

The expectation that the action of phenylthiocarbimide on the α - and β -hydrazones would lead to phenylthiocarbamyldhydrazones corresponding with the phenylcarbamyldhydrazones described in our previous communication has not been fulfilled, the product from both hydrazones being the same.

EXPERIMENTAL.

The Isomeric Camphorquinonephenylhydrazones,



In order to avoid the possibility of transformation being effected by the acetic acid which is free in the usual method of producing phenylhydrazones, the diketone and the base were allowed to undergo condensation in ethereal solution. The phenylhydrazine was first purified by Fischer's method, namely, crystallisation from chilled ether, which yields it in the form of a grey, silvery powder, remaining dry at temperatures below 20° . About 60 grams of camphorquinone were dissolved in 250 c.c. of warm ether, to which was added the calculated amount of phenylhydrazine diluted with 50 c.c. of the solvent. The action which immediately set in was moderated by cooling, and after an interval of sixteen hours the hard, crystalline mass was collected, and the mother liquor allowed to evaporate without being heated, depositing a further crop of crystals embedded in a deep yellow oil. In our earlier experiments,

the oil was submitted to distillation in steam, because this treatment was found to separate the β -phenylhydrazone effectively from its less volatile isomeride, but the process is a tedious one, about twelve hours being occupied by the passage of 5 grams. In consequence of this, later procedure consisted in extracting the residue with small quantities of cold petroleum, which leaves most of the α -phenylhydrazone undissolved, and, on evaporation, yields the β -phenylhydrazone as a yellow, viscous mass containing a small proportion of the isomeride. The quantities of crude materials obtained in this fashion correspond with 85 per cent. of the α -compound, and 10 per cent. of the isomeric substance.

Purification of the α -phenylhydrazone was effected by rapid successive crystallisations from hot benzene or alcohol, and trouble has been taken to procure a colourless specimen; this, however, could not be accomplished, even by working throughout in artificial light. Animal charcoal has no influence on the colour of good specimens, and the device employed for decolorising benzenediazo- ψ -semicarbazinocamphor (Trans., 1906, **89**, 229), namely, addition of zinc dust to a cold solution in glacial acetic acid, was without influence on the colour of the solution. It is our opinion therefore that camphorquinone- α -phenylhydrazone is coloured, and in its palest forms, derived by precipitation with water from an alcoholic solution, the shade of yellow is faintly green, very similar, in fact, to that of camphorquinone- β -hydrazone described in our paper already quoted. It should be noted, however, that the appearance of the α -phenylhydrazone depends largely on the compactness of the mass observed; thus crystals which have separated from a solution in petroleum appear less coloured than those from alcohol until withdrawn from the liquid, because the amount dissolved is very small, and the deposit is comparatively bulky.

The want of agreement between the melting points recorded by various chemists who have worked with this substance is explained by the facility with which transformation into the more fusible isomeride takes place. The temperatures are, in chronological order, 170—171° (Claisen and Manasse), 180° (Betti), 180—181° (Lapworth and Hann), 180° (Robertson), and 178—180°, occasionally 183° (Auwers). Some years ago, a specimen obtained by one of us as a by-product of the interaction of $\alpha\alpha$ -bromonitrocamphor and phenylhydrazine (Trans., 1902, **81**, 869) was stated to melt at any temperature between 183° and 190° according to the rate of heating, and this observation we are able to confirm; if the substance is not absolutely dry, or if the temperature is raised very slowly, the conversion into the β -phenylhydrazone makes sufficient headway to furnish, locally, a solvent for the less fusible form, so

that under these conditions one is taking the melting point of the α -compound mixed with its solution in the β -modification. If the purified α -phenylhydrazone is plunged into a bath at 175 — 180° , the temperature may be raised slowly to 190° before fusion is complete.

The specific rotatory power of our specimen in absolute alcohol was somewhat lower than that recorded by Lapworth, being $[\alpha]_D 431^\circ$ in 1 per cent. solution (by volume); the corresponding figures for pyridine and nitrobenzene were 435.5° and 453.9° respectively.

Camphorquinone- β -phenylhydrazone.—Suggested by the relative volatility of the isomeric camphorquinonehydrazones, our first attempts to prepare the missing β -phenylhydrazone consisted in heating the α -phenylhydrazone at its melting point during several minutes, and then passing a current of steam through the gummy product, when there slowly distilled a yellow oil which was extracted with ether and, after drying, allowed to remain in the vacuum desiccator until solid. More convenient procedure, however, consists in heating the α -phenylhydrazone in quantities of about 10 grams until all has melted, and the temperature of the bath has reached 210° , when the cooled product is extracted with a small quantity of light petroleum, filtered from about 8 per cent. of the α -phenylhydrazone, and the solvent evaporated without being heated. On stirring the viscous residue, it solidifies very rapidly, especially if sown with a few crystals of the substance. The hard, crystalline phenylhydrazone melts at 36° , and has been crystallised from chilled light petroleum or from diluted alcohol without undergoing alteration of melting point or of optical activity:

0.4510 gave 1.2361 CO_2 and $0.3187 \text{ H}_2\text{O}$. $\text{C} = 74.75$; $\text{H} = 7.91$.

0.2375 „ 22.4 c.c. N_2 at 18° and 757 mm. $\text{N} = 10.93$.

$\text{C}_{16}\text{H}_{20}\text{ON}_2$ requires $\text{C} = 75.00$; $\text{H} = 7.81$; $\text{N} = 10.93$ per cent.

The most convenient way to purify the new phenylhydrazone is to dissolve 10 grams in about 100 c.c. of alcohol, add 15 c.c. of water, and then cool the solution to the neighbourhood of -15° , when vigorous stirring brings about the separation of half the material in minute, yellow crystals; by slow separation from the mother liquor, these take the form of lustrous, transparent, six-sided plates. The colour of the dry substance is much deeper than that of the α -phenylhydrazone, approximating more to that of camphorquinone itself; its solubility is very much greater, 10 grams being dissolved readily by 5 grams of petroleum (b. p. 40 — 50°), or by 10 c.c. of cold absolute alcohol. Solutions of the β -phenylhydrazone are much brighter yellow than those of the isomeride except in the case of nitrobenzene, where this comparison is inverted.

The melting point is not depressed by admixture with the α -phenylhydrazone, and if equal quantities of the two substances are used, the temperature may be raised to about 170° before fusion is complete; in this respect therefore the behaviour of the two phenylhydrazones resembles that of the hydrazones and their other derivatives, and also that of the two modifications of isonitroso-camphor.

The specific rotatory power of the β -phenylhydrazone when dissolved in alcohol has been determined with many different specimens, prepared both by distillation in steam and by extraction with petroleum; the uniformity of this constant at $[\alpha]_D^{375^{\circ}}$ for a 1 per cent. solution (by volume) establishes the individuality of the new isomeride. In benzene, pyridine, and nitrobenzene, the respective constants are 369.5° , 395.5° , and 420.5° . Addition of ethereal ferric chloride to solutions of the phenylhydrazones does not give the least justification for regarding either as an enolic modification of the other.

Interconversion of the Isomeric Phenylhydrazones.

As already stated, the α -phenylhydrazone is rapidly converted into the β -modification when fused; the converse change is brought about by carrying the temperature of liquefied β -phenylhydrazone to the melting point of the less fusible form, and the proportion of isomerides in the resulting mixture is independent of the identity of the initial material. The composition of the mixture depends on the temperature at which the transformation is effected, and the foregoing conditions, being more favourable to the existence of the β -modification, do not illustrate in the most satisfactory manner the conversion of this form into the α -isomeride, the percentage of which does not exceed 10 per cent. If alcoholic solutions of the two phenylhydrazones are separately boiled under reflux during five hours, however, the proportion of the α -derivative in the resulting equilibrium mixture is raised to nearly 40 per cent., which, in view of the sparing solubility of the material, may be recognised without difficulty.

In order to place the interconversion of the isomeric phenylhydrazones upon a quantitative basis, a series of polarimetric observations has been made with solutions containing one gram of each modification in 100 c.c. of absolute alcohol, these being separately heated at 63° during a period of twelve hours. The initial rotation having been recorded, each solution was distributed among a number of similar tubes; these were withdrawn at suitable intervals and cooled to the original temperature (16°) as rapidly as possible, the contents being transferred to the instrument in a

3-dm. tube without delay. The following readings were thus obtained:

Time in Minutes.	α -Phenylhydrazone.			β -Phenylhydrazone.		
	α_D .	Weight transformed.	$k_1 + k_2$.	α_D .	Weight transformed.	$k_1 + k_2$.
0	12°56'	—	—	11°15'	—	—
30	12 46	0·0990	0·0026	11 20·5	0·0544	0·0021
60	12 37·5	0·1832	0·0027	11 25·5	0·1040	0·0021
90	12 29	0·2674	0·0029	11 29·5	0·1435	0·0021
120	12 23	0·3268	0·0029	11 33	0·1782	0·0021
180	12 15	0·4060	0·0028	11 40	0·2475	0·0023
360	12 3	0·5248	0·0026	11 50	0·3465	0·0023
480	11 59·5	0·5590	0·0026	11 51·5	0·3614	0·0020
720	11 57	0·5851	0·0025	11 55	0·3961	0·0022
∞	11 56	0·5940	—	11 56	0·4060	—
	Mean.....		0·0027	Mean.....		0·00215

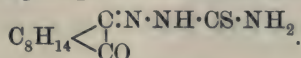
In the foregoing table the figures recorded in the columns headed $k_1 + k_2$ are calculated from the equation:

$$k_1 + k_2 = \frac{1}{t} \log \frac{x_0 - x_\infty}{x_t - x_\infty},$$

where k_1 and k_2 are the velocity-constants of the isomeric change in the two directions, and x_0 , x_∞ , and x_t are the observed rotations initially, finally, and at time t respectively. This is the relation employed by Küster, Trey, Lowry, Hudson, Tubandt, and others in dealing with problems of similar character, and it will be noticed that whilst the values for $k_1 + k_2$ agree among themselves for the same phenylhydrazone, they are not identical for the two phenylhydrazones. Although this disagreement should not occur, other workers have encountered the same peculiarity, sometimes in a more pronounced form, and it is probably due to some disturbing influence affecting the first few observations; this view is confirmed by calculations based on the later readings only, when $k_1 + k_2$ is nearly the same for both directions.

These results are embodied in the curves on p. 488.

The Camphorquinonethiosemicarbazones,

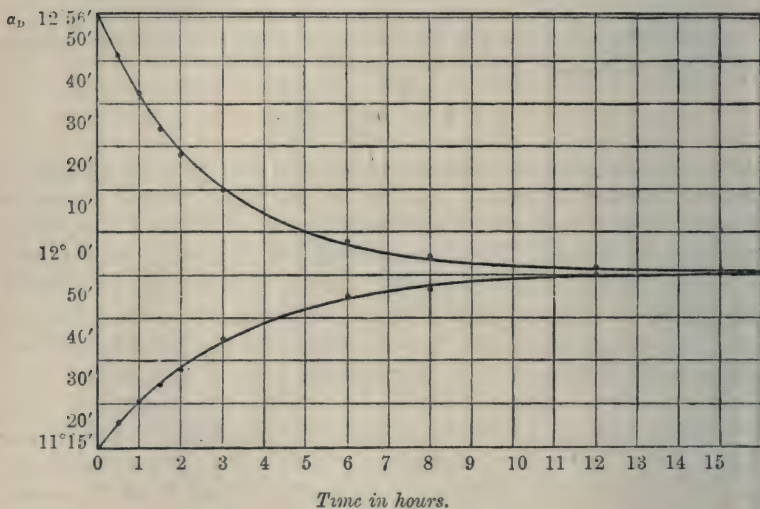


Thiosemicarbazide dissolved in 5 parts of boiling water was added to one molecular proportion of camphorquinone in 3 parts of hot acetic acid, when the yellow colour disappeared, action being complete after fifteen minutes under reflux; diluting the cold liquid with water precipitated an oil which rapidly crystallised, the yield being 95 per cent. of that required by theory. On recrystallisation from water or carbon disulphide, the appearance of pale yellow prisms, having ill-defined faces, and melting indefinitely at

122—137°, suggested the occurrence of mixed crystals containing both forms, and this was confirmed by the failure of repeated crystallisation from other solvents, such as benzene, ethyl acetate, chloroform, and glacial acetic acid, to yield a definite product. On dissolving the crystals in alcohol, however, and scratching the sides of the vessel, there separated the α -thiosemicarbazone in colourless, lustrous crystals, containing 1 mol. C_2H_6O , and the same material arose on evaporating the mother liquor on the water-bath or in the vacuum desiccator, so that the β -thiosemicarbazone could not be isolated:

0.4968 lost 0.0794 during half an hour at 120°. Loss = 15.98.

$C_{11}H_{17}ON_3S + C_2H_6O$ requires $C_2H_6O = 16.14$ per cent.



Interconversion of the camphorquinonephenylhydrazones: 1 per cent. solution, 3-dcm. tube.

Upper curve: α -Phenylhydrazone. Lower curve: β -Phenylhydrazone.

The substance, when free from alcohol, is very pale greenish-yellow, and melts at 174°:

0.1290 gave 19.8 c.c. N_2 at 19° and 757 mm. $N = 17.36$.

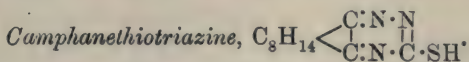
0.2679 „ 0.2593 $BaSO_4$. $S = 13.29$.

$C_{11}H_{17}ON_3S$ requires $N = 17.57$; $S = 13.39$ per cent.

Camphorquinone- α -thiosemicarbazone is readily soluble in warm alcohol, benzene, or chloroform, but is insoluble in petroleum. Alkali hydroxides readily form orange-yellow solutions, from which carbon dioxide precipitates the substance unchanged, but it dissolves also in hot sodium carbonate, and crystallises as the liquid cools;

continued heating of a solution in alkali hydroxide gives rise to camphor. A 1 per cent. solution (by volume) in chloroform gave α_D $9^\circ 26'$ in a 3-dcm. tube, whence $[\alpha]_D$ 314.4° .

Transformation of the α -thiosemicarbazone into the β -modification takes place when the substance is heated at the melting point, being followed by removal of water and consequent production of the thiotriazine; it has not been possible therefore to produce the β -thiosemicarbazone by the process which was applied to the β -phenylhydrazone. Nor could the second isomeride be separated by alkalis, as in the case of semicarbazones themselves, because when a mixture of the α - and β -thiosemicarbazones is treated with these agents, the β -modification is transformed so rapidly into the thiotriazine that there is no opportunity to separate it from the α -isomeride, which, however, is not convertible into the thiotriazine.



The most convenient source of the thiotriazine is the crude product of condensation between camphorquinone and thiosemicarbazide, which contains approximately 50 per cent. of the β -thiosemicarbazone; on dissolving this mixture in alkali hydroxide and saturating the solution with carbon dioxide, the α -thiosemicarbazone is precipitated, whilst the filtrate yields the thiotriazine on acidification with dilute hydrochloric acid. When recrystallised from alcohol, it forms fern-like aggregates of lustrous, yellow prisms, melting at 207° :

0.1673 gave 0.1763 $BaSO_4$. $S=14.46$.

$C_{11}H_{15}N_3S$ requires $S=14.47$ per cent.

The thiotriazine dissolves readily in hot methyl and ethyl alcohols, benzene, chloroform, pyridine, or ether, but only sparingly in hot petroleum or water; it is soluble in alkali hydroxides, alkali carbonates, and ammonia, but is insoluble in dilute acids. A 1 per cent. solution (by volume) in chloroform gave α_D $-2^\circ 12'$ in the 3-dcm. tube, whence $[\alpha]_D$ -73.3° .

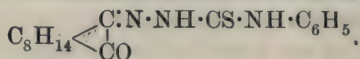
Derivatives of the thiotriazine with heavy metals are produced very easily. Mercuric chloride gives a voluminous, white precipitate, which dissolves in hot water, and separates in slender, colourless needles on cooling; silver nitrate and copper acetate give pale yellow and green precipitates respectively.

Conversion into Camphaneoxytriazine.—An attempt to replace sulphur by heating the thiotriazine with water and mercuric oxide was unsuccessful; the yellow colour disappeared, but the filtered liquid deposited crystals of the above-mentioned mercury salt. On adding a solution of ammoniacal silver oxide which contained only

just sufficient ammonia to a solution of the thiotriazine (1 gram) in hot water (200 c.c.), however, the pale yellow silver derivative gradually became dark on further heating, and ultimately changed into a black, granular mass of silver sulphide; after four hours under reflux, the filtered liquid was saturated with sodium chloride and extracted with ether, which deposited the oxytriazine.

The acetyl derivative of the oxytriazine was obtained from the thiotriazine by heating it with acetic anhydride under reflux during one hour.

Camphorquinonephenylthiocarbamylhydrazone,



The same derivative was obtained alike by heating the α -hydrazone with the calculated amount of phenylthiocarbimide in alcohol under reflux during three hours, and by action of the thiocarbimide on the β -hydrazone in benzene during twenty-four hours at the laboratory temperature. Recrystallisation from hot benzene gave small, lustrous, pale yellow leaflets, melting at 184° :

0.0988 gave 11.5 c.c. N_2 at 18° and 764 mm. $\text{N} = 13.52$.

0.2916 „ 0.2134 BaSO_4 . $\text{S} = 10.05$.

$\text{C}_{17}\text{H}_{21}\text{ON}_3\text{S}$ requires $\text{N} = 13.39$; $\text{S} = 10.16$ per cent.

The substance dissolves somewhat readily in hot alcohol, benzene, chloroform, or ethyl acetate, but is insoluble in petroleum; a solution in hot sodium hydroxide is deep yellow. The 1 per cent. solution (by volume) in chloroform gave $\alpha_D^{20} 7.47'$ in the 3-dcm. tube, whence $[\alpha]_D^{25} 259.4^\circ$. An attempt to produce it by heating camphorquinone-thiosemicarbazone with aniline was not successful.

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LIX.—*The Constituents of Withania somnifera.*

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

THE plant *Withania somnifera*, Dunal (Nat. ord. *Solanaceae*), occurs in South Africa, where it is found in gardens and waste places, and is known under the Kaffir name of *ubu-Vumba*. It is also a native of the west coast of India, and is said to be common along the shores of the Mediterranean. The plant is described in De Candolle's *Prodromus*, Vol. 13, Part I, p. 453, and has been recorded by

J. Medley Wood in a List of the Flora of Natal (*Trans. South African Phil. Soc.*, 1908, **18**, Part II, 197), while a more extended description of its characters and uses is given in Smith's "Contribution to South African Materia Medica," pp. 145, 166, and in the "Pharmacographia Indica," Vol. II, p. 566. Although various medicinal properties have been attributed to the plant, it is particularly stated to act as a sedative and hypnotic (*Amer. J. Pharm.*, 1891, **63**, 77), and this action has been considered by Trebut (*The Lancet*, 1886, **1**, 467) to be due to the presence of an alkaloid, which was provisionally designated by him "somniaferine." Inasmuch as nothing of a definite nature has been recorded respecting this alkaloid or the other constituents of the plant, it seemed desirable to subject it to a more complete examination, and the results are summarised at the end of this paper.

EXPERIMENTAL.

The material used for the present investigation was received directly from South Africa, and consisted of both the root and the overground portion of the plant.

I. Examination of the Root.

A small portion of the root was tested for the presence of an alkaloid, with a positive result.

Fifty grams of the ground material were subsequently extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—40°)	extracted	0.22 gram	=0.44	per cent.
Ether	"	0.35 "	=0.70	" "
Chloroform	"	0.23 "	=0.46	" "
Ethyl acetate	"	0.35 "	=0.70	" "
Alcohol	"	2.15 "	=4.30	" "

Total..... 3.30 grams or 6.60 per cent.

For the purpose of a complete examination, 18.37 kilograms of the ground root were extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, there remained a dark-coloured, viscid extract, which amounted to 2.7 kilograms.

Distillation of the Extract with Steam: Separation of an Essential Oil.

The whole of the above extract was mixed with water, and the mixture distilled in a current of steam for several hours. The distillate, which contained a small amount of an essential oil, was

shaken with ether, the ethereal liquid being washed, dried, and the solvent removed. The essential oil thus obtained possessed a light brown colour, a pungent odour, and amounted to 1.2 grams, being thus equivalent to about 0.006 per cent. of the weight of the root.

Non-volatile Constituents of the Extract.

After the above-described operation, there remained in the distillation flask a dark-coloured, aqueous liquid (A), and a considerable quantity of a black resin (B). These products were separated by filtration, and the resin thoroughly washed with water, the washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid was concentrated under diminished pressure to a convenient volume, and then repeatedly extracted with ether. A small amount (4.5 grams) of a viscid, brown oil was thus removed, which, however, with the exception of traces of a weak base, yielded nothing of interest.

The aqueous liquid was next shaken repeatedly with amyl alcohol. This solvent extracted a considerable quantity of a yellow, amorphous product, which, on exposure to the atmosphere, rapidly absorbed moisture, and became glutinous. This yellow solid could not be obtained crystalline, nor could any crystalline derivative be prepared from it. It was not glucosidic.

The aqueous liquid was subsequently treated with a slight excess of basic lead acetate, when a voluminous, light brown precipitate was obtained. The lead precipitate, which contained nothing of an alkaloidal nature, was examined in the usual way, but yielded only indefinite substances, giving the reactions for tannin. The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the lead, and the mixture filtered. The concentrated filtrate was yellow in colour, and contained a considerable quantity of sugar, since it readily yielded *d*-phenylglucosazone, melting and decomposing at 210°. On heating the liquid with alkali hydroxide, it developed ammonia, and it also yielded precipitates with the usual alkaloid reagents, but these reactions were evidently due to soluble protein products, since the alkaline liquid, when extracted with either chloroform or amyl alcohol, yielded nothing of a definitely alkaloidal nature.

Examination of the Resin (B).

The resin amounted to 502 grams, being thus equivalent to about 2.7 per cent. of the weight of the root. It was digested with hot

alcohol, the solution poured upon purified sawdust, and the dried mixture extracted successively in a Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This was a dark-coloured, soft solid, which amounted to 138 grams. It was heated in a reflux apparatus with an excess of an alcoholic solution of potassium hydroxide, the greater portion of the alcohol then removed, water added, and the alkaline mixture extracted with ether. On evaporating the solvent, a quantity (37 grams) of a brown, viscid product was obtained, which was found to contain some basic substance. It was therefore re-dissolved in ether, and the ethereal solution shaken with dilute hydrochloric acid. The acid liquid was then carefully neutralised with sodium carbonate, when a colourless precipitate, amounting to about 0.1 gram, was deposited. This substance, when recrystallised from dilute alcohol, separated in colourless, glistening leaflets, melting at 116° , and was found to be identical with the base, $C_{12}H_{16}N_2$, subsequently to be described in connexion with the examination of the ether extract of the resin. As will be shown later, it is probable that the above compound is not originally present in the resin, but was formed from an alkaloidal constituent by the treatment with alcoholic potassium hydroxide.

Isolation of Hentriacontane, $C_{31}H_{64}$, and a Phytosterol, $C_{27}H_{46}O$.

The ethereal solution, which had been shaken with hydrochloric acid for the removal of the base, as described above, was washed, dried, and the solvent evaporated. The residue was then fractionally crystallised from a mixture of ethyl acetate and alcohol. The more sparingly soluble deposits, when crystallised from ethyl acetate, were obtained in glistening leaflets, melting at $67-68^{\circ}$, and proved to be hentriacontane. (Found, $C=85.2$; $H=14.5$. Calc., $C=85.3$; $H=14.7$ per cent.)

After the removal of the greater part of the hentriacontane in the above fractionation, the mother liquors gradually deposited a small quantity of a substance in flat plates. This was purified by recrystallisation from ethyl acetate, and it then melted at $135-136^{\circ}$:

0.1113 * gave 0.3420 CO_2 and 0.1202 H_2O . $C=83.8$; $H=12.0$.

$C_{27}H_{46}O$ requires $C=83.9$; $H=11.9$ per cent.

This substance was evidently a phytosterol, and it gave the colour reaction of that class of compounds.

* Anhydrous substance.

*The Fatty Acids.**Isolation of Cerotic Acid, $C_{26}H_{52}O_2$.*

The alkaline, aqueous solution of potassium salts, which had been extracted with ether for the removal of the unsaponifiable material, as above described, was acidified with sulphuric acid, and extracted with ether. On evaporating the ethereal solution, it yielded 15 grams of a dark green, soft solid, which evidently contained a considerable amount of resinous matter. The latter was separated by washing with petroleum, in which the resin was insoluble. The mixed fatty acids obtained from the petroleum washings were converted into their methyl esters, and the latter distilled under diminished pressure. Two fractions were collected, the one distilling at $205\text{--}230^\circ/28\text{ mm.}$, and the other above $230^\circ/28\text{ mm.}$ The latter fraction, consisting of a wax-like solid, yielded, on hydrolysis, an acid which, on recrystallisation from alcohol, separated in clusters of colourless leaflets, melting at $71\text{--}72^\circ$, and was identified as cerotic acid (Found, $C=78.7$; $H=13.2$. Calc., $C=78.8$; $H=13.1$ per cent.), the somewhat low melting point being probably due to a slight impurity.

The above-mentioned fraction, which distilled at $205\text{--}230^\circ/28\text{ mm.}$, contained a considerable proportion of unsaturated esters. The entire fraction was therefore hydrolysed, and the resulting fatty acids separated by means of their lead salts into saturated and unsaturated portions. The saturated acids, amounting to 5.5 grams, were crystallised from alcohol, and thus separated into two fractions of different solubilities. Each of these fractions melted at $52\text{--}54^\circ$, but they possessed neutralisation values of 210 and 201 respectively, and it was thus evident that the saturated acids consisted of a mixture of palmitic and stearic acids.

The unsaturated acids, which amounted to 4.8 grams, were distilled under diminished pressure, when they passed over at $220\text{--}240^\circ/20\text{ mm.}$ An analysis and a determination of the iodine value gave the following results:

0.1391 gave 0.3916 CO_2 and 0.1462 H_2O . $C=76.8$; $H=11.7$.

0.1711 absorbed 0.2260 iodine. Iodine value = 132.1.

$C_{18}H_{34}O_2$ requires $C=76.6$; $H=12.1$ per cent. Iodine value = 90.1.

$C_{18}H_{32}O_2$ „ $C=77.1$; $H=11.4$ „ Iodine value = 181.4.

These results indicate that the unsaturated acids consisted of a mixture of oleic and linolic acids in approximately equal proportions.

*Ethereal Extract of the Resin.**Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.*

The ether extract of the resin was a black, brittle solid, amounting to 42.7 grams. It was digested with a large volume of ether, when about 4 grams of a light green, solid substance remained undissolved. The latter was collected, and purified by several crystallisations from pyridine containing a little water, when it was obtained in colourless, microscopic needles, melting and decomposing at 290—300°:

0.1103 gave 0.2929 CO_2 and 0.1021 H_2O . $C = 72.4$; $H = 10.3$.

$C_{23}H_{40}O_4$ requires $C = 72.6$; $H = 10.5$ per cent.

When the substance was dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, a transient pink colour, changing to blue and then to green, was produced. The compound also yielded an acetyl derivative, melting at 164—165°, and it was thus definitely identified as ipuranol.

The ethereal solution from which the sparingly soluble ipuranol had been removed, as above described, was extracted successively with aqueous ammonium carbonate, sodium carbonate, and sodium hydroxide. These extracts, however, on acidification, yielded only resinous material. On evaporating the greater portion of the ether, a small quantity of a crystalline compound separated, which, when purified by crystallisation from a mixture of alcohol and chloroform, separated in thin, colourless needles, melting and decomposing at 300°. It was found to be identical with the new compound, withaniol, $C_{25}H_{34}O_5$, which was obtained in larger amount from the chloroform extract of the resin.

Isolation of an Alkaloidal Principle.

The ethereal filtrate from the above-described crystalline substance contained a compound which gave precipitates with the usual alkaloid reagents. The alkaloidal principle was not soluble in dilute acids, but was extracted from the ethereal liquid by repeatedly shaking with concentrated hydrochloric acid. The acid liquids were then carefully neutralised with sodium carbonate, when an amorphous solid was precipitated, which was taken up with chloroform. The chloroform extract, after washing and drying, yielded 1.5 grams of a weak, gum-like base, which could not be obtained in a crystalline state. It gave a yellow, amorphous gold salt, melting and decomposing at 185°.

Action of Potassium Hydroxide on the Alkaloid. Isolation of a Crystalline Base, $C_{12}H_{16}N_2$.

A portion of the above-described alkaloid was heated for an hour with an alcoholic solution of potassium hydroxide. The alcohol was then removed, water added, and the alkaline liquid extracted with ether. The ethereal solution was then shaken with dilute hydrochloric acid, and the acid liquid neutralised with aqueous sodium carbonate, when a small amount (0.2 gram) of a colourless solid was precipitated. This substance was crystallised from dilute alcohol, and was thus obtained in colourless, glistening leaflets, melting at 116° :

0.0792 gave 0.2230 CO_2 and 0.0597 H_2O . $C = 76.8$; $H = 8.4$.

0.0655 „ 8.5 c.c. moist N_2 (over KOH) at 14° and 760 mm.
 $N = 15.3$.

$C_{12}H_{16}N_2$ requires $C = 76.6$; $H = 8.5$; $N = 14.9$ per cent.

The above-described substance would thus appear to possess the empirical formula $C_{12}H_{16}N_2$, and, as it differs in its properties from any substance of this formula which has hitherto been recorded, it is evidently a new compound.

The *base*, $C_{12}H_{16}N_2$, is readily soluble in alcohol, ethyl acetate, ether, chloroform, or benzene, but only sparingly soluble in light petroleum or hot water. It is neutral towards litmus, but is easily dissolved by an excess of dilute mineral acids. When heated in an ignition tube, it first melts, and then sublimes unchanged.

The *hydrochloride* was prepared by adding to an ethereal solution of the base a drop of concentrated hydrochloric acid. A crystalline solid was thus deposited, which, when recrystallised from a mixture of ether and alcohol, separated in thin, colourless needles, sintering at 190° , and melting at 201° . The *picrate* crystallised from hot water, in which it is only moderately soluble, in silky, yellow needles, melting at 171° .

After the removal of the crystalline base from the product of the above reaction, the alkaline liquid yielded, on acidification, a small quantity of a solid substance, which, however, could not be obtained crystalline.

Chloroform Extract of the Resin.

Isolation of a New Monohydric Alcohol, Withaniol, $C_{25}H_{33}O_4 \cdot OH$.

The portion of the resin extracted by chloroform was relatively large, amounting to 123 grams. It was redissolved in chloroform, and the solution extracted with aqueous ammonium carbonate, sodium carbonate, and sodium hydroxide, each of which removed

some amorphous, resinous material. The chloroform solution was then washed, dried, and the solvent removed, when a viscid, brown residue was obtained, which, on agitation with alcohol, deposited a colourless, crystalline compound. This compound, amounting to 5 grams, was collected, and recrystallised from a mixture of chloroform and alcohol, when it separated in colourless needles, which sintered at 285° and completely decomposed at 305° :

0.1081 gave 0.2866 CO_2 and 0.0816 H_2O . $\text{C}=72.2$; $\text{H}=8.4$.

0.1022 „ 0.2703 CO_2 „ 0.0750 H_2O . $\text{C}=72.1$; $\text{H}=8.2$.

The molecular weight of the substance was determined by the cryoscopic method:

0.3170, in 28.16 nitrobenzene, gave $\Delta t = -0.191^{\circ}$. M.W. = 412.

$\text{C}_{25}\text{H}_{34}\text{O}_5$ requires $\text{C}=72.5$; $\text{H}=8.2$ per cent. M.W. = 414.

No compound of the empirical formula $\text{C}_{25}\text{H}_{34}\text{O}_5$, possessing properties identical with those of the above substance, has hitherto been described. It is therefore proposed to designate the new compound *withaniol*, with reference to the generic name of the plant from which it has been obtained.

Withaniol, $\text{C}_{25}\text{H}_{34}\text{O}_5$, is readily soluble in chloroform, only moderately so in alcohol, and practically insoluble in ether or light petroleum. It dissolves in cold concentrated hydrochloric acid, and is precipitated unchanged on the addition of water. It undergoes some change when heated with alkalis in the presence of alcohol, since the solution becomes deep red, and deposits, on acidification, a red, amorphous precipitate. When dissolved in a mixture of acetic anhydride and chloroform, and a drop of concentrated sulphuric acid subsequently added, a pink coloration appears, which gradually changes to a straw-yellow colour.

Withaniol is optically active, a determination of its rotatory power giving the following result:

0.3745, made up to 20 c.c. with chloroform, gave $\alpha_D + 3^{\circ}15'$ in a 2-dm. tube, whence $[\alpha]_D + 91.2^{\circ}$.

Withaniol contains no methoxy-group, but the presence of one hydroxyl group was proved by the formation of a monoacetyl derivative.

Acetylwithaniol, $\text{C}_{25}\text{H}_{33}\text{O}_5 \cdot \text{CO} \cdot \text{CH}_3$.—This derivative was prepared by heating *withaniol* for some time with an excess of acetic anhydride. On cooling the solution, the *acetyl* compound was deposited in the form of colourless, prismatic needles. After recrystallisation from acetic anhydride, it began to melt at 280° , and at 300° became completely decomposed:

0.1032 gave 0.2675 CO_2 and 0.0750 H_2O . $\text{C}=70.7$; $\text{H}=8.1$.

0.1122 „ 0.2920 CO_2 „ 0.0832 H_2O . $\text{C}=71.0$; $\text{H}=8.2$.

$\text{C}_{25}\text{H}_{33}\text{O}_5 \cdot \text{CO} \cdot \text{CH}_3$ requires $\text{C}=71.1$; $\text{H}=7.9$ per cent.

Ethyl Acetate Extract of the Resin.

This was a black, brittle solid, amounting to 26.8 grams. It was heated for several hours with dilute sulphuric acid in aqueous alcohol, when, after removing the alcohol, an amorphous resin separated, and a yellow, aqueous liquid was obtained which readily reduced Fehling's solution. The presence of sugar in the aqueous liquid was confirmed by the formation of *d*-phenylglucosazone, melting and decomposing at 210°. It is thus evident that the ethyl acetate extract of the resin was glucosidic in character.

Alcohol Extract of the Resin.

This resin amounted to 105 grams, and consisted of a hard, black solid. A preliminary examination having indicated the presence of a glucosidic substance, the whole of the resin was heated for several hours with dilute sulphuric acid in aqueous alcohol. After the removal of the alcohol, the mixture was distilled in a current of steam, but no volatile product of hydrolysis was obtained. There then remained in the distillation flask a quantity of resin and a reddish-brown, aqueous liquid, which was separated by filtration. The resin yielded nothing crystalline, but the aqueous liquid, when rendered alkaline by means of sodium hydroxide, deposited about 1 gram of a dark brown, gelatinous product. This was collected, found to contain nitrogen, and to possess weakly basic properties. It was, however, of a very indefinite character, and could not be obtained crystalline, nor could any crystalline salt be prepared from it. When heated with aqueous potassium hydroxide, a strong ammoniacal odour was developed.

The aqueous liquid, from which the above-described basic substance had been removed, readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting and decomposing at 205°. It is thus apparent that at least a portion of the alcohol extract of the resin was of a glucosidic nature.

II. Examination of the Leaves and Stems.

As a preliminary experiment, a small portion of the ground material was tested for the presence of an alkaloid, and with a positive result.

For the purpose of a complete examination, 6.97 kilograms of the dried leaves and stems were ground, and extracted by continuous percolation with hot alcohol. The greater part of the alcohol was then removed, the residual extract (2.24 kilograms) mixed with water, and the mixture distilled in a current of steam. The

distillate contained a very small quantity (0.2 gram) of an essential oil, possessing a strong, pungent odour.

After the above-described operation, there remained in the distillation flask a brown, aqueous liquid, containing a quantity of resin. These products were separated by decantation, and the resin well washed with boiling water, the washings being added to the main volume of aqueous liquid.

Examination of the Aqueous Liquid.

The aqueous liquid was concentrated under diminished pressure to a convenient bulk, then repeatedly extracted with ether, and finally with amyl alcohol. These solvents, however, removed only small quantities of gummy material, which, in each case, was found to contain a trace of a weak amorphous base. The latter, although responding to the usual tests for an alkaloid, was very indefinite in character, and yielded no crystalline salt. No glucosidic substance was present.

The aqueous liquid which had been extracted with the above-mentioned solvents was subsequently treated with an excess of basic lead acetate, which removed tannin and colouring matter. The filtrate from the basic lead acetate precipitate was deprived of lead and concentrated under diminished pressure to a small volume, when, on cooling, a considerable quantity of potassium nitrate was deposited. The filtrate from the latter still gave a precipitate with alkaloid reagents, and also contained some sugar, since it readily yielded *d*-phenylglucosazone, decomposing at 205°. The aqueous liquid was finally rendered alkaline and extracted successively with ether and chloroform, but these solvents removed only very small quantities of a gummy, basic substance, which yielded no crystalline derivative.

Examination of the Resin.

The resin was a dark green powder, and amounted to 624 grams. It was dissolved in hot alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This extract was a dark green, soft solid, amounting to 67 grams. It was dissolved in ether, and the solution shaken with both dilute and strong hydrochloric acid, but no basic substance was thus removed.

Isolation of Hentriacontane, $C_{31}H_{64}$, and a Phytosterol, $C_{27}H_{46}O$.

The above-mentioned ethereal liquid was next distilled for the removal of the solvent, and the residue heated with an alcoholic solution of potassium hydroxide. After the removal of the alcohol, water was added, and the alkaline liquid completely extracted with ether. The ethereal extract yielded 26 grams of a semi-solid product, which was fractionally crystallised from ethyl acetate, when a colourless compound, separating in glistening leaflets and melting at 68° , was obtained. This substance, amounting to 5 grams, was identified as hentriacontane (Found, $C=85.1$; $H=14.7$. Calc., $C=85.3$; $H=14.7$ per cent.).

The mother-liquors from the above crystallisations were united, the solvent removed, and the residue fractionally distilled under diminished pressure. The lower-boiling fractions contained a considerable quantity of hentriacontane, but the final fraction, after several crystallisations from hot alcohol, yielded a compound crystallising in flat plates, which melted at 133° , and gave the colour reaction of the phytosterols:

0.0883 gave 0.2720 CO_2 and 0.0940 H_2O . $C=84.0$; $H=11.8$.

$C_{27}H_{46}O$ requires $C=83.9$; $H=11.9$ per cent.

This substance was thus proved to be a phytosterol, and it was apparently identical with that obtained from the root.

*The Fatty Acids.**Isolation of Cerotic Acid, $C_{26}H_{52}O_2$.*

The alkaline liquid from which the above-mentioned hentriacontane and phytosterol had been removed was acidified with sulphuric acid, and the precipitated fatty acids taken up with ether. The ethereal solution, on the evaporation of the solvent, yielded a semi-solid residue of fatty acids, which were converted into their methyl esters, and the latter then fractionally distilled under diminished pressure. The greater portion passed over at $205-215^{\circ}/12$ mm., but a small fraction was collected above $215^{\circ}/12$ mm., and a considerable quantity of non-volatile resinous material remained in the distillation flask. The fraction distilling above $215^{\circ}/12$ mm. solidified in the receiver, and, when recrystallised from alcohol, was obtained in glistening leaflets, melting at $56-57^{\circ}$. This product consisted of methyl cerotate (m. p. 60°), since on hydrolysis it yielded an acid which separated from ethyl acetate in stellar aggregates of fine needles, melting at $76-77^{\circ}$ (Found, $C=78.6$; $H=13.3$. Calc., $C=78.8$; $H=13.1$ per cent.).

The fraction of methyl esters distilling at 205—215°/12 mm. was hydrolysed, and the regenerated acids separated by means of their lead salts into saturated and unsaturated portions. The saturated acids were found to melt at 49—51°, and to possess a neutralisation value of 205°. After one crystallisation from alcohol, the melting point was 51—53° and the neutralisation value 207°. It was thus evident that the saturated acids consisted of a mixture of palmitic and stearic acids, which possess neutralisation values of 219 and 198 respectively.

The unsaturated acids were distilled under diminished pressure, when they passed over at 220—235°/15 mm. An analysis and a determination of the iodine value gave the following results:

0.1033 gave 0.2912 CO₂ and 0.1075 H₂O. C=76.9; H=11.6.

0.1306 absorbed 0.2086 iodine. Iodine value=159.7.

C₁₈H₃₄O₂ requires C=76.6; H=12.1 per cent. Iodine value=90.1.

C₁₈H₃₂O₂ „ C=77.1; H=11.4 „ „ Iodine value=181.4.

The unsaturated acids would thus appear to have consisted of a mixture of oleic and linolic acids, the latter preponderating.

Ethereal Extract of the Resin.

Isolation of Ipuranol, C₂₃H₃₈O₂(OH)₂.

This extract was obtained in the form of a light green powder, amounting to 156 grams. On digesting the extract with ether, it was observed that a portion of it was very sparingly soluble. This was therefore separated by filtration from the more readily soluble portion, which amounted to 60 grams, and consisted of chlorophyll and indefinite amorphous substances. The portion sparingly soluble in ether was subsequently digested with hot alcohol, when a small quantity of a light green solid remained undissolved. The latter was collected, and, after crystallisation from dilute pyridine, was found to decompose at 285—290°, and to give the colour reaction of ipuranol. Its complete identification was effected by means of the acetyl derivative, which melted at 164—165°, and when mixed with a known specimen of acetylipuranol the melting point remained unchanged.

Isolation of a New Monohydric Alcohol, Somnirol, C₃₂H₄₃O₆·OH.

The above-mentioned alcoholic solution of the sparingly soluble portion of the ether extract of the resin was heated to boiling, and sufficient water added to produce a faint cloudiness. On cooling, a quantity of an oily resin separated, which gradually became semi-solid. This was collected and put aside for subsequent examination. By the further cautious addition of water

to the hot mother-liquors, the greater portion of the oleo-resinous material was removed, after which a crystalline substance began to be deposited. The latter was then purified by several recrystallisations from dilute alcohol, when it was obtained in colourless, prismatic needles in an amount of 3 grams:

0.5981, dried at 110° , lost $0.0364 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 6.1$.

0.0975* gave 0.2542 CO_2 and $0.0748 \text{ H}_2\text{O}$. $\text{C} = 71.1$; $\text{H} = 8.5$.

0.1126* „ 0.2882 CO_2 „ $0.0834 \text{ H}_2\text{O}$. $\text{C} = 71.0$; $\text{H} = 8.4$.

0.1136* „ 0.2968 CO_2 „ $0.0844 \text{ H}_2\text{O}$. $\text{C} = 71.3$; $\text{H} = 8.2$.

$\text{C}_{32}\text{H}_{44}\text{O}_7 \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.2$ per cent.

$\text{C}_{32}\text{H}_{44}\text{O}_7$ requires $\text{C} = 71.1$; $\text{H} = 8.1$ per cent.

The molecular weight of the substance was determined by the cryoscopic method with the following result:

0.5496*, in 31.52 nitrobenzene, gave $\Delta t = -0.225^{\circ}$. $\text{M.W.} = 542$.

$\text{C}_{32}\text{H}_{44}\text{O}_7$ requires $\text{M.W.} = 540$.

No substance identical with the above compound appears to have hitherto been described. It is therefore proposed to designate the new compound *somnirol*, with reference to its alcoholic properties and the specific name of the plant from which it has been isolated.

Somnirol, $\text{C}_{32}\text{H}_{48}\text{O}_6 \cdot \text{OH}$, is very soluble in alcohol, ethyl acetate, or chloroform, only moderately soluble in benzene, and very sparingly so in ether. It crystallises from dilute alcohol with two molecules of water of crystallisation, which are expelled at 110° , but are again rapidly absorbed when the anhydrous substance is exposed to the atmosphere. The behaviour of the substance on heating is characteristic, inasmuch as it partly melts at about 155° with effervescence and immediate resolidification, and then finally fuses with evolution of gas at 205° .

A determination of the optical rotatory power of somnirol gave the following result:

0.1796,* made up to 25 c.c. with chloroform, gave $\alpha_D + 0^{\circ}30'$ in a 2-dcm. tube, whence $[\alpha]_D + 34.8^{\circ}$.

Somnirol contains no methoxyl, and, as shown below, only one hydroxyl group. In order to obtain some further information respecting the character of the substance, a portion of it was heated with decinormal alcoholic potassium hydroxide:

0.2002, heated for 20 minutes, neutralised 0.0222 KOH .

$\text{KOH} = 11.1$ per cent.

0.2271, heated for one hour, neutralised 0.0275 KOH .

$\text{KOH} = 12.1$ per cent.

$\text{C}_{32}\text{H}_{44}\text{O}_7$, to neutralise 1 mol. KOH , requires $\text{KOH} = 10.4$ per cent.

With the object of isolating, if possible, the products of the

* Anhydrous substance.

above reaction, a quantity (0.5 gram) of somnirol was heated for a short time with alcoholic potassium hydroxide. The alcohol was then removed and water added, but no precipitation ensued, nor could any product be isolated from the alkaline solution by extraction with ether or chloroform. The alkaline liquid, on acidification, deposited a gelatinous precipitate, which, after collecting and drying, was found to be only imperfectly soluble in alkalis, and almost insoluble in the ordinary organic solvents. From these results it may be concluded that somnirol contains at least one lactonic grouping.

Acetylsomnirol, $C_{32}H_{43}O_7 \cdot CO \cdot CH_3$.—This compound was prepared by heating somnirol for an hour with acetic anhydride, the greater portion of the latter being then removed by distillation, and water added, when the *acetyl* derivative was precipitated as an oil, which gradually became solid. The product was collected, dried in a vacuum over sulphuric acid, and dissolved in hot benzene, from which it was deposited in colourless, torpedo-shaped crystals. The latter contained benzene of crystallisation, which was not lost on keeping the compound for some time in a vacuum over sulphuric acid, and was only very slowly expelled on heating at 100° . When heated in a capillary tube, the air-dried substance begins to change at about 115° , and apparently melts at 125° with evolution of gas. Heated to 110° on a watch-glass, the substance gradually melts, bubbles of gaseous benzene are evolved, and it then resolidifies to a hard, brittle, transparent mass. On recrystallising the latter from benzene, the original compound, containing that solvent, was obtained:

0.1178 gave 0.3157 CO_2 and 0.0859 H_2O . $C=73.1$; $H=8.1$.

$C_{32}H_{43}O_7 \cdot CO \cdot CH_3, C_6H_6$ requires $C=72.7$; $H=7.9$ per cent.

The benzene-free acetyl derivative was next analysed:

0.1369 gave 0.3510 CO_2 and 0.0994 H_2O . $C=69.8$; $H=8.1$.

0.0801 „ 0.2050 CO_2 „ 0.0586 H_2O . $C=69.8$; $H=8.1$.

$C_{32}H_{43}O_7 \cdot CO \cdot CH_3$ requires $C=70.1$; $H=7.9$ per cent.

Isolation of a New Dihydric Alcohol, Somnitol, $C_{33}H_{44}O_5(OH)_2$.

The dilute alcoholic mother-liquors remaining after the separation of the somnirol, as above described, still contained a considerable amount of substance in solution. On removing the alcohol in a current of steam, an oily substance was deposited, which gradually solidified. The solid was collected, dried in a vacuum over sulphuric acid, and then digested with ethyl acetate. This treatment removed the remaining somnirol, and left a sparingly soluble compound, which was recrystallised from alcohol. It separated from

this solvent in thin, hair-like needles, which sintered at 240° , and melted and decomposed at about 250° . The yield of this substance was 4 grams:

0.4704, dried at 110° , lost $0.0310 \text{ H}_2\text{O}$. $\text{H}_2\text{O}=6.6$.

0.1160* gave 0.3037 CO_2 and $0.0898 \text{ H}_2\text{O}$. $\text{C}=71.4$; $\text{H}=8.6$.

0.1071* „ 0.2805 CO_2 „ $0.0830 \text{ H}_2\text{O}$. $\text{C}=71.4$; $\text{H}=8.6$.

$\text{C}_{33}\text{H}_{46}\text{O}_7 \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=6.1$ per cent.

$\text{C}_{33}\text{H}_{46}\text{O}_7$ requires $\text{C}=71.5$; $\text{H}=8.3$ per cent.

A molecular-weight determination by the cryoscopic method gave the following result:

0.2454,* in 33.80 nitrobenzene, gave $\Delta t = -0.092^{\circ}$. M.W.=553.

$\text{C}_{33}\text{H}_{46}\text{O}_7$ requires M.W.=554.

No compound of the above formula appears to have previously been described. It is therefore proposed to designate the substance *somnitol*, with reference to its alcoholic character and the specific name of the plant from which it has been obtained.

Somnitol is practically insoluble in water, and only moderately soluble in hot absolute alcohol. It dissolves readily in chloroform and in dilute alcohol, separating from the latter solvent with 2 molecules of water. The compound is optically active, a determination of its rotatory power giving the following result:

0.3040,* made up to 25 c.c. with chloroform, gave $\alpha_D +0^{\circ}31'$ in a 2-dm. tube, whence $[\alpha]_D +21.2^{\circ}$.

When *somnitol* is heated with alkali hydroxides in alcoholic solution it slowly undergoes change, and the liquid acquires a deep red colour, but even after prolonged heating with concentrated alkali a part of the compound was recovered unaltered. The reaction is therefore not comparable with that which takes place when *somnirol* is similarly treated, since in the latter case no trace of unchanged substance can be detected, even after a few minutes' heating with the alkali.

Somnitol contains no methoxyl, but was found to possess two hydroxyl groups, since it readily yields a diacetyl derivative.

Diacetylsomnitol, $\text{C}_{33}\text{H}_{44}\text{O}_7(\text{CO}\cdot\text{CH}_3)_2$.—This compound was prepared by heating *somnitol* with acetic anhydride for an hour. On concentrating the solution, an *acetyl* derivative separated in colourless prisms, which, after recrystallisation from acetic anhydride, melted and decomposed at $270\text{--}275^{\circ}$. It was practically insoluble in cold acetic anhydride or alcohol, but readily soluble in chloroform:

0.1127 gave 0.2866 CO_2 and $0.0841 \text{ H}_2\text{O}$. $\text{C}=69.4$; $\text{H}=8.3$.

0.1056 „ 0.2693 CO_2 „ $0.0782 \text{ H}_2\text{O}$. $\text{C}=69.6$; $\text{H}=8.2$.

$\text{C}_{33}\text{H}_{44}\text{O}_7(\text{CO}\cdot\text{CH}_3)_2$ requires $\text{C}=69.6$; $\text{H}=7.8$ per cent.

* Anhydrous substance.

Isolation of an Acidic, Hydrolytic Product: Withanic Acid,
 $C_{29}H_{45}O_6 \cdot CO_2H$.

The oily resin which had separated from the alcoholic solution of the ether extract of the resin by the first addition of water, as above described, was next examined, but no crystalline compound could be directly isolated from it. It was therefore heated for a short time with an alcoholic solution of potassium hydroxide, the alcohol then removed, and the product of hydrolysis extracted successively with ether and chloroform, which, however, removed nothing. On acidifying the alkaline liquid, a gelatinous precipitate was formed, the greater part of which was insoluble in organic solvents, but a small portion was soluble in hot alcohol, from which it crystallised in colourless, tetrahedral prisms, melting and decomposing at 226° :

0.1124, dried at 110° , lost 0.0038 H_2O . $H_2O = 3.1$.

0.1136* gave 0.2796 CO_2 and 0.0904 H_2O . $C = 67.1$; $H = 8.8$.

$C_{30}H_{46}O_8 \cdot H_2O$ requires $H_2O = 3.3$ per cent.

$C_{30}H_{46}O_8$ requires $C = 67.4$; $H = 8.6$ per cent.

This substance was readily soluble in alkalis, including ammonium carbonate, and when titrated with a decinormal alcoholic solution of sodium hydroxide gave the following result:

0.2060 neutralised 3.8 c.c. $N/10$ -NaOH. M.W. (monobasic acid) = 542.

$C_{29}H_{45}O_6 \cdot CO_2H$ requires M.W. = 534.

As the above-described acid is evidently a new compound, it is proposed to designate it *withanic acid*.

Withanic acid, $C_{30}H_{46}O_8$, is very sparingly soluble in ether, chloroform, or benzene, and only moderately soluble in boiling alcohol. Its *methyl* ester, prepared by heating the substance with methyl alcohol in presence of concentrated sulphuric acid, was very soluble in alcohol or acetone, but could be crystallised from a mixture of acetone and benzene, when it separated in hard, crystalline nodules, sintering at 240° , and decomposing with effervescence at 255° .

Chloroform Extract of the Resin.

This consisted of a light green powder, which amounted to 212 grams. As nothing could be directly isolated from this material, it was heated with dilute sulphuric acid in aqueous alcohol. On subsequently rendering the liquid alkaline, about 1 gram of an almost colourless, glutinous solid separated, which

* Anhydrous substance.

was found to contain nitrogen, but which could not be obtained crystalline nor did it yield any crystalline salt.

The chloroform extract of the resin was also tested for the presence of a glucoside, but with a negative result.

Ethyl Acetate and Alcohol Extracts of the Resin.

The ethyl acetate extract of the resin amounted to only 10 grams. It was found to contain some glucosidic material, since on heating with dilute sulphuric acid in aqueous alcohol it yielded a sugar from which *d*-phenylglucosazone (m. p. 205°) was prepared.

The alcohol extract of the resin, consisting of a hard, brittle solid, amounted to 94 grams. It was glucosidic in character, and on heating for several hours with dilute sulphuric acid in aqueous alcohol it also yielded a small amount of an indefinite basic substance, the properties of which were very similar to those of the substance obtained from the chloroform extract of the resin.

Summary.

The material employed for this investigation represented the entire plant of *Withania somnifera*, Dunal (Nat. ord. *Solanaceae*), and was obtained directly from South Africa. The root and the overground portion of the plant, consisting of the leaves and stems, were separately examined.

Preliminary tests, conducted with both portions of the plant, indicated the presence of an alkaloid.

I. Constituents of the Root.—An alcoholic extract of the root, when distilled with steam, yielded a very small amount of an essential oil. The portion of the extract which was soluble in water contained, besides indefinite, amorphous substances, a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 210°).

The portion of the extract which was insoluble in water consisted chiefly of a black resin, and amounted to about 2·7 per cent. of the weight of the root. From this resin the following definite substances were isolated: hentriacontane, $C_{31}H_{64}$; a phytosterol, $C_{27}H_{46}O$ (m. p. 135—136°); a mixture of fatty acids, consisting of palmitic, stearic, cerotic, oleic, and linolic acids; ipuranol, $C_{23}H_{38}O_2(OH)_2$; a new monohydric alcohol, *withaniol*, $C_{25}H_{33}O_4 \cdot OH$, decomposing at 305°, and having $[\alpha]_D + 91 \cdot 2^\circ$; and an amorphous, alkaloidal principle, which, on treatment with alkalis, yielded a crystalline base, $C_{12}H_{16}N_2$ (m. p. 116°).

II. Constituents of the Leaves and Stems.—An alcoholic extract of this material, when submitted to distillation with steam, yielded a very small amount of an essential oil. The portion of the extract which was soluble in water contained, besides tannin and colouring

matter, a sugar yielding *d*-phenylglucosazone (m. p. 205°), and a considerable quantity of potassium nitrate.

The portion of the extract which was insoluble in water consisted chiefly of resinous material, and was obtained in the form of a dark green powder. This resin was found to contain a number of substances which had also been isolated from the root of the plant, such as hentriacontane, a phytosterol, $C_{27}H_{46}O$ (m. p. 133°), a mixture of fatty acids, and ipuranol. In addition to these, however, it yielded the following compounds: a new monohydric alcohol, *somnirol*, $C_{32}H_{43}O_6 \cdot OH$, decomposing at 205° and having $[\alpha]_D + 34.8^\circ$; a new dihydric alcohol, *somnitol*, $C_{33}H_{44}O_5(OH)_2$, decomposing at about 250°, and having $[\alpha]_D + 21.2^\circ$; and an acidic, hydrolytic product, *withanic acid*, $C_{29}H_{45}O_6 \cdot CO_2H$ (m. p. 226°), the *methyl* ester of which decomposed at 255°.

Inasmuch as the *Withania somnifera*, unlike some other solanaceous plants, had been found to contain no mydriatic alkaloid, it was deemed of interest to ascertain whether the sedative or hypnotic properties attributed to it could be confirmed. For this purpose, some tests were kindly conducted for us at the Wellcome Physiological Research Laboratories by Drs. H. H. Dale and P. P. Laidlaw, to whom our thanks are due. It was thus ascertained that alcoholic extracts, representing about 7 grams of the root and 3 grams of the leaves and stems respectively, when administered to a dog had no perceptible effect. The hypodermic injection of the alkaloidal principle obtained from the root likewise produced in a dog no symptom of narcosis or other definite result.

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LX.—The Constancy of Water of Crystallisation in Hydrated Salts. Part I.

By HERBERT BRERETON BAKER and GEORGE HENRY JOSEPH ADLAM.

THE use of salts containing water of crystallisation for accurate work, such as the determination of atomic weights, has been a subject of discussion for many years. According to Richards (*Zeitsch. physikal. Chem.*, 1904, **46**, 216), such salts always contain an excess of water, supposed to be occluded in some way in the mass of the crystal. Marckwald (*Ber.*, 1907, **40**, 4730) published a paper in 1907 on the atomic weight of tellurium, in which he

concluded that the true atomic weight was below that of iodine, solely on the evidence obtained from the decomposition of telluric acid ($\text{H}_2\text{TeO}_4, 2\text{H}_2\text{O}$). This work was criticised by one of us (Baker, *Chem. News*, 1908, **97**, 209), both on general grounds, and also because a long series of experiments with the same substance had pointed to the impossibility of obtaining the crystals of constant composition. Marckwald * has recently withdrawn his assertion of the low atomic weight, since by using a more trustworthy method for the determination he has obtained results which confirm the number found by other investigators. It was in reference to telluric acid that this work was begun, but other cases have been studied.

* In the cases which we have investigated, it has been found that there is, as Richards proved for barium chloride, an excess of water over the calculated amount. Richards (*loc. cit.*) considers that this water is occluded in cavities in the crystal, since by reducing the substance to varying degrees of fineness, the excess of water was appreciably diminished, the process of powdering having opened up some of the larger cavities. Mallet (*Phil. Trans.*, 1880, **171**, 1003), however, attributes a similar loss of water in the case of ammonium alum to the heat generated in crushing the crystals, and the work of Carey Lea (*Phil. Mag.*, 1892, [v], **34**, 46; 1894, [v], **37**, 31) has shown that the enormous mechanical energy which is brought to bear on a substance in powdering is able to bring about the decomposition of substances of far greater stability than crystalline hydrates.

* Marckwald and Foizik (*Ber.*, 1910, **43**, 1710). In this paper, objection is taken to the method of determination of the atomic weight by heating tellurium dioxide with sulphur, the loss of sulphur dioxide being measured. The authors state that sulphur trioxide is formed as well as the dioxide. This assertion seems unlikely, since excess of sulphur and free tellurium are present, but we have thought it worth while to repeat experiments. In two experiments, 6 grams and 8 grams of highly purified tellurium dioxide were mixed with excess of purified sulphur, silver leaf being packed in the exit tube. The air having been displaced by nitrogen, the mixture was heated and the gas passed through a dilute acid solution of barium chloride which had been previously boiled to remove dissolved oxygen. A guard tube of distilled water was attached to the bulbs of barium chloride solution, and in these circumstances the solution remained perfectly clear in both experiments, showing that no sulphur trioxide was formed. When the solution of barium chloride, saturated with sulphur dioxide, was exposed to the air, precipitation of barium sulphate was observed in ten minutes. The German chemists also found that a temperature of 200° was necessary, whilst one of us and Bennett (*Trans.*, 1907, **91**, 1849) found that it began at 130° . The lower temperature has been confirmed by inserting a thermometer in the heated mixture of sulphur and tellurium dioxide. If the tellurium dioxide has been previously heated to a very high temperature, it is probable that the reaction would require a higher temperature before it began.

Our object was to devise a method by which both occluded water and adhering solvent would be removed without taking away any of the water of crystallisation. In order to do this, a desiccating agent must be found, the vapour tension of which is less than that of the occluded mother liquor, but not less than the tension of the water of crystallisation, and, secondly, crystals must be permeable to water vapour.

A suitable desiccating agent is found in a mixture obtained by partly dehydrating some of the substance to be dried. If such a mixture is placed in a closed space which contains also some of the same hydrated salt with mother liquor, the vapour tension will be always that of the fully hydrated salt, and the mother liquor will evaporate, leaving crystals of definite and constant weight.

The principle of the method was first suggested by Andreae (*Zeitsch. physikal. Chem.*, 1891, **7**, 241) for the isolation of hydrates of salts. It was used by Walker and Beveridge (*Trans.*, 1907, **91**, 1797) in the preparation of *p*-toluidine monohydrate. While our work was in progress, it was again used by Cumming (*Trans.*, 1910, **97**, 593) in the isolation of the hydrates of sodium carbonate, and also by Guye and Tsakalotos (*J. Chim. Phys.*, 1909, **8**, 3), whose object was the same as ours, namely, the preparation of hydrates in such a condition that they could be used for atomic-weight determinations.

With regard to the permeability of crystals to water vapour, there are two possibilities. If crystals are to be regarded as built up of crystals of molecular dimensions which are not in absolute contact, it is probable that not only water vapour, but other gases may pass through them. On the other hand, if a crystal be made into a partition between an atmosphere which is saturated with water vapour and a dried atmosphere, dehydration may take place at one surface of the crystal, and the dehydrated layer take up water from the next layer. This process being repeated, the net result will be that water will pass through the crystal from the wet to the dried atmosphere, although the crystal may show no signs of the change which has taken place. We incline to the view that the passage of water through crystals takes place in the second way, since we find that, in the cases examined, hydrated crystals are permeable to water vapour, but anhydrous crystals are impermeable. In order to test whether crystals are permeable to gases, as they would be on the first of the above hypotheses, the following experiments were made. A U-shaped tube was bent so that the limbs were close together. On one end of the tube a flat-bottomed open cup was blown, in which a crystal was cemented by paraffin wax. Mercury was introduced into the bend, the tube was

exhausted, and the open end was sealed. The levels of the mercury in the two limbs of the U-tube were observed with a cathetometer. When air-dried crystals were used, it was found that the mercury was depressed in the limb sealed by the crystal, but never to an extent greater than the maximum tension of aqueous vapour at the temperature of the room. A crystal of potassium chlorate (anhydrous), dried over sulphuric acid, showed no depression of the mercury column, while a crystal of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) showed a depression of about 6 mm., equal to the tension of the water of crystallisation of the salt. Hence we see that under the pressure of an atmosphere, air will not pass through the mass of a crystal, and since in some cases water vapour does so, its passage must take place by some such process as that outlined above.

Drying of Telluric Acid.

Marckwald states that 15 grams of telluric acid, when kept in a vacuum over phosphoric oxide, lost only 0.3 milligram in two months. Since this statement appeared to be at variance with the previous experience of one of us, the point was investigated in the following way.

Ten grams of the recrystallised acid were weighed in a silica dish against a counterpoise dish of the same material. Both were kept in a vacuum desiccator over phosphoric oxide. Weighings were made at frequent intervals over a period of five months. For the first two days a considerable loss in weight was noticed, no doubt due to surface water. There was a continual decrease in the loss of water, but this loss was still going on when the experiment was stopped. The average daily loss for the last month was 0.1 milligram. In order to investigate further if water was still present in the free state, the dried acid was analysed. Portions were weighed in a dried stoppered silica tube, using a similar silica tube as counterpoise. To the first tube was fitted, by very careful grinding, a connexion made of Jena glass, by means of which a current of air, dried by phosphoric oxide, was enabled to sweep through all traces of water into a bulb, which itself was connected by a ground joint to a U-tube containing phosphoric oxide, the bulb and the U-tube being weighed together. It may be noted that the ground connexion between silica and glass is a very satisfactory arrangement when lubricators are, as in this case, inadmissible. The glass expands more than the silica, so that the joint becomes tighter as the temperature rises. The weights are corrected to vacuum standard. The percentage of water calculated ($\text{Te}=127.50$) is 23.546. The calculated total loss is 30.516:

No.	Telluric acid, grams.	Water collected, gram.	Total loss, gram.	Water found, per cent.	Total loss found, per cent.	Difference of	
						water calc. and found, per cent.	total loss calc. and found, per cent.
1.	3·06816	0·72668	0·94048	23·683	30·654	+0·137	+0·138
2.	2·52287	0·56974	0·77251	23·653	30·620	+0·108	+0·104
3.	3·26298	0·77020	0·99722	23·604	30·562	+0·058	+0·046
4.	3·04471	0·71840	0·93019	23·595	30·551	+0·035	+0·047
1.	Telluric acid dried for one month over solid potassium hydroxide.						
2.	"	"	"	"	"	"	"
3.	"	"	"	"	"	"	"
4.	"	"	"	"	"	"	"

It will be seen that with these different amounts of drying there is always an excess of water in the crystallised telluric acid, and this excess is sensibly equal to the excess in the total loss of weight on decomposition, assuming the atomic weight of tellurium to be 127·5.* It is seen also that this excess of water is not removed by exposure of the acid to the drying of phosphoric oxide in a vacuum for six months. It will be seen later that telluric acid crystals are apparently impermeable to water vapour, and hence the excess of water is retained in the interior of the crystals. We have found that crystals containing true water of crystallisation will allow of the passage of water vapour through them, and we are of opinion that these experiments uphold the view suggested by Gutbier, and supported by Marckwald, that the formula of this acid should be written H_6TeO_6 , and not $H_2TeO_4 \cdot 2H_2O$. This view is further strengthened by the fact, discovered by Berzelius, that if the substance is dehydrated until it has the composition H_2TeO_4 , the white powder thus obtained can be kept in water for some time without re-hydration. We have repeated this experiment, and we find that after six months' keeping in water, less than a quarter has passed into solution.

In order to show the difference of behaviour of telluric acid and that of a substance containing true water of crystallisation, the following experiment was performed. A weighed quantity of re-crystallised copper sulphate, which had been dried to constant weight over partly dehydrated copper sulphate, was placed in a vacuum desiccator containing some of the same salt, which was completely dehydrated. The salt was weighed at intervals:

Date.	Weight of salt.	Change.
Aug. 18th	3·43590	-0·00060
Aug. 26th	3·43530	-0·01225
Oct. 11th	3·42305	

Thus, crystallised copper sulphate loses its water of crystallisation

* From the members obtained in these experiments, the ratio of $TeO_2 : O$ is obtained: (1) 100 : 10·042; (2) 100 : 10·020; (3) 100 : 10·016; (4) 100 : 10·049, giving a mean result 100 : 10·032, which gives for the atomic weight of tellurium 127·49.

with considerable rapidity when placed in an atmosphere dried by the anhydrous salt, which is not a very powerful dehydrating agent. The hydrated salt, also, was found to lose practically all its water of crystallisation when dried over phosphoric oxide.

Drying of Hydrated Salts over the same Salts Partly Dehydrated.

The substances used in the following experiments were carefully purified by recrystallisation, and finally obtained in small crystals by the sudden cooling of a saturated solution. The substances, contained either in vessels of silica or in light stoppered weighing bottles of a wide, shallow pattern, were taken while still moist, and left exposed to the desiccating action of the partly dehydrated salt contained in a vacuum desiccator. Weighings were made at regular intervals until no further loss could be detected even after leaving the substance some considerable time. A counterpoise which was always exposed to the same conditions was used in weighing. It was found to be necessary to readmit air very slowly into the vacuum desiccator before weighing, and also to subject the air to some preliminary process of drying by passing it through a sulphuric acid worm, and then through a long tube containing a mixture similar to that in the desiccator. For the drying agent, the commercial substance without any purification was used. The preliminary dehydration was so regulated that some of the unchanged hydrate always remained in the desiccating material. In all the experiments, it was carefully ascertained that the drying mixture had remained efficient throughout; a large quantity was always used, and, furthermore, it was renewed at frequent intervals.

Barium Chloride.

The specimen of barium chloride, after careful purification, remained for about six months in a vacuum over partly dehydrated barium chloride (other experiments being then in progress). A portion of this product was then taken and weighed several times in succession, being in the meantime subject to the treatment described in the previous section:

Date	Weight of salt.	Change in Weight.
Jan. 8th ..	3·57008	— 0·00015
„ 9th ..	3·56993	— 0·00004
„ 11th ..	3·56989	— 0·00001
„ 12th ..	3·56992	— 0·00003
„ 13th ..	3·56993	— 0·00000
„ 15th ..	3·56993	

The first loss, which is considerable, may probably be attributed to adsorption of moisture during transference to a weighing bottle.

The percentage of water of crystallisation in this product was found to be 14·772, a result which, whilst agreeing with other determinations, is above the calculated amount, 14·747.

Thus during the long period of drying, the salt not only did not lose any of its water of crystallisation, but still contained an appreciable excess.

We were, however, able to obtain a specimen of barium chloride with the theoretical percentage of water of crystallisation by the following process. The crystallised salt was first completely dehydrated and finely powdered. It was then left in a vacuum in the presence of partly dehydrated sodium sulphate, and kept there as long as it continued to take up water. Then, in order to remove any adsorbed water, it was placed in another desiccator over partly dehydrated barium chloride, and left there until by three weighings in succession, with four days between each weighing, it was ascertained that the substance had reached a constant weight.

1·84103 grams of this product, on drying to constant weight at 250—270°, lost 0·27155 gram. This corresponds with a percentage of 14·750 instead of 14·747 ($Ba=137\cdot37$).

Copper Sulphate, $CuSO_4\cdot5H_2O$.

This salt is known to form lower hydrates with vapour tensions lower than that of the pentahydrate. Two specimens of the salt were used, one in small crystals, and the other finely powdered in a mortar, so that it might be seen if the stability of the hydrate was affected by the mechanical breaking of the crystals. On leaving in an atmosphere dried by partly dehydrated copper sulphate, the weighed salts attained constancy of weight in three weeks, and no further change of more than 0·01 milligram was observed during the next eight weeks.

Potash Alum, $K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$.

This salt was chosen on account of the large amount of water which it contains, and the high tension of the water vapour. Two portions were taken, one in small crystals, and the other finely powdered. The salts were not subjected to preliminary drying, but on keeping over the partly dehydrated salt, most of the surface water was found to have disappeared in a week's time, and after a month's drying in this way, the change in weight from week to week did not amount to more than 0·01 milligram on 2·5 grams of salt. As this very small change was sometimes positive and sometimes negative, it may be concluded that it represents the error in weighing.

Oxalic acid ($C_2H_2O_4\cdot 2H_2O$) was treated in a similar way, but its

weight showed a progressive diminution throughout the period of drying. The loss in the third month was found to be due to the volatilisation of the acid at the ordinary temperature, feathery crystals being deposited on the edges of the silica dish.

Permeability of Crystals to Water Vapour.

In these experiments a very thin glass flask, of about 5 c.c. capacity, was used, which contained phosphoric oxide. The mouth of the flask was expanded into a shallow cup, in which the crystal was cemented with paraffin wax. For weighing, a similar flask, closed by a similar crystal, but not containing phosphoric oxide, was used as a counterpoise. The crystals used were grown for the purpose, and were free from cracks and flaws. After weighing, the two flasks were placed in an atmosphere containing water vapour of less than the maximum tension at the ordinary temperature, so as to avoid the possibility of the condensation of liquid water on the crystals or the glass. Since the flasks were air-tight, the increase of weight of the one containing phosphoric oxide represents the amount of water which had diffused through the crystal. An experiment was first made with a potassium chlorate crystal, which is, of course, anhydrous. The crystal was 0.86 mm. thick. On June 21st, the flask weighed 7.05803 grams, in the following September, 7.05800 grams, showing that water did not pass through the crystal.

A similar experiment with a telluric acid crystal, 1.62 mm. in thickness, gave the following result:

Date.	Weight of flask and crystal, grams.
May 19th	1.29842
„ 23rd	1.29838
Sept. 9th	1.29837
Oct. 22nd	1.29839

Hence it is evident that water does not pass through this substance.

With a crystal of copper sulphate 1.93 mm. thick there was a gain in weight of the flask containing phosphoric oxide of 0.04431 gram between March 8th and July 5th. The daily increase was comparatively steady, for the first forty days amounting to 0.00034 gram. During the next thirty days the daily increase was 0.00037 gram. Another crystal of copper sulphate, 2.31 mm. thick, gave similar results, although the average daily increase was less, 0.00011 gram.

Barium Chloride.

Crystal 2.56 mm. thick.

Date.	Weight, grams.	Total increase, gram.	Days.	Average increase per day, gram.
May 28th.....	11.01774	0.00061	26	0.00002
June 23rd	11.01835	0.00105	38	0.00003
July 5th	11.01879	0.00536	54	0.00010
„ 21st.....	11.02310			

Potassium Ferrocyanide.

Water passing through in a direction parallel to the principal plane of cleavage.

Crystal 4.13 mm. thick.

I. June 10th	11.33188	0.01085	20	0.00054
„ 30th	11.34273	0.02299	29	0.00079
July 9th	11.35487	0.05847	43	0.00136
„ 23rd	11.39035			

Crystal 4.10 mm. thick.

II. June 9th	3.52139	0.00550	21	0.00025
„ 30th	3.52689	0.01040	30	0.00033
July 9th	3.53179	0.02580	44	0.00059
„ 23rd.....	3.54719			

Potassium Ferrocyanide.

Water passing through at right angles to the principal plane of cleavage.

Crystal 0.74 mm. thick.

Date.	Weight, grams.	Increase, gram.	Days.	Average increase per day, gram.
I. June 9th	7.68214	0.00022	12	0.00002
„ 21st.....	7.68236	0.00589	28	0.00021
July 7th	7.68803	0.04126	44	0.00094
„ 23rd	7.72340			

Crystal 0.88 mm. thick.

II. June 9th	8.66113	0.00140	21	0.00007
„ 30th	8.66253	0.01297	28	0.00046
July 7th	8.67140	0.04721	44	0.00107
„ 23rd	8.70834			

Sodium Thiosulphate.

Crystal 6.6 mm. thick.

June 23rd	12.72692	0.00765	7	0.00109
„ 30th	12.73457	0.02974	16	0.00186
July 9th	12.75666	0.08847	26	0.00340
„ 19th	12.81539			

In order to compare more conclusively the behaviour of hydrated and anhydrous crystals, plates of anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) of the same thickness were mounted in a similar way in the necks of bulbs containing phosphoric oxide. They were exposed with the counterpoise to moist air for three months. The anhydrite bulb showed no increase in weight, whilst that containing gypsum increased by 7 milligrams. The gypsum crystal showed dehydration on the under side, the upper surface being still bright.

The transference of water in the case of hydrated crystals is accompanied by the dehydration of the crystal on the side nearer the phosphoric oxide. The dehydrating action was in all cases confined to the under surface and to that part of it which was not protected by the paraffin wax, so that the sealing of the crystal was in no way interfered with by the dehydration. The mode of transference of water vapour through these crystals is rather difficult to decide, but the following experiment seems to show that the dehydration which takes place is apparently a necessity.

Crystals of sodium sulphate were placed in a flask, which was closed by a crystal of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and the flask was weighed against another flask also closed by a crystal of copper sulphate, but containing no sodium sulphate. Both flasks were then placed in a desiccator over anhydrous copper sulphate:

Thickness of crystal = 1.28 mm.

Weight on Aug. 9th C + 0.09009 gram
 „ „ Oct. 11th C + 0.09008 „

Hence, although anhydrous copper sulphate can in ordinary circumstances take up water freely from sodium sulphate, yet under the conditions of the above experiment, the sodium sulphate shows no sign of loss of water during a period of two months, which points to the fact that partial dehydration of the crystal must precede the passage of water vapour through it.

These permeability experiments have an important bearing on the question of occluded water. If, as our experiments seem to show, partial dehydration must precede the passage of water vapour through the crystal, then the method of drying over the partly dehydrated salt can have no effect on the occluded water. This is confirmed both by the experiment which shows that partly dehydrated copper sulphate could not take up water from sodium sulphate when the latter was contained in a flask closed by a crystal of copper sulphate, and by the fact that barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, even after six months' exposure in a vacuum to the action of the partly dehydrated salt, still contained an excess of

water agreeing very well with determinations by Richards and Marignac (*loc. cit.*).

While these experiments were in progress, a paper was published by Guye and Tsakalotos (*J. Chim. Phys.*, 1909, **7**, 215), in which a similar method of drying was described. Barium chloride, in quantities of about 2 grams, was dried at $34\cdot5^{\circ}$ in the presence of about 40 grams of anhydrous barium chloride, to which a few drops of distilled water had been added. The distilled water was added in order to ensure the presence of the hydrate $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ in the drying agent.

Their results obtained for the ratio $\text{BaCl}_2\cdot 2\text{H}_2\text{O} : \text{BaCl}_2$ are very concordant. The mean percentage of water of crystallisation in the residue was found to be 14·6765, which is below the amount (14·747) calculated from the atomic weights given in the international table for 1911. The percentage in our experiments was 14·772.

From the experience gained in the previous experiments, we are inclined to think that the mere sprinkling of a large amount of barium chloride, spread over the bottom of crystallising dishes, with a few drops of distilled water does not ensure the effective presence of the highest hydrate. Under such conditions, we think that the salt must have been slightly dehydrated in the process of drying.

Conclusions.

1. It is possible to determine the true weight of a salt containing water of crystallisation with the same degree of accuracy as that which is usually attained when weighing other substances.

2. If compounds containing water of crystallisation are of definite composition, then the products of constant weight, which are obtained by exposing moist crystals to the action of the products of their own partial dehydration, cannot contain less than the theoretical quantity of water.

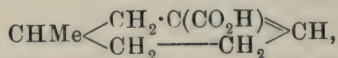
3. Anhydrous crystals will not allow water vapour to pass through them, but salts with water of crystallisation allow this passage with varying degrees of freedom.

4. It is possible to obtain barium chloride with the theoretical percentage of water of crystallisation by re-hydrating the anhydrous salt in the presence of a substance of higher vapour tension. The work is being continued in order to find if this method of obtaining salts with their true amount of water of crystallisation is a general one.

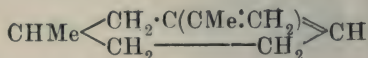
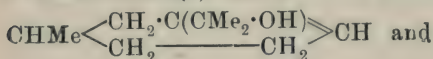
LXI.—*Experiments on the Synthesis of the Terpenes.*
Part XVI. Resolution of dl-1-Methyl- Δ^3 -cyclohexene-3-carboxylic Acid and Synthesis of the d- and l-Modifications of Δ^3 -m-Menthenol(8) and $\Delta^{3:8(9)}$ -m-Menthadiene.

By BERNARD DUNSTAN WILKINSON LUFF (1851 Exhibition Scholar of University College, Nottingham) and WILLIAM HENRY PERKIN, jun.

IN a recent communication (Trans., 1910, **97**, 2149, 2151) a method is described by which *dl*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid:



may be obtained with comparative ease, and the possession of considerable quantities of this acid enabled us to prepare Δ^3 -*m*-menthenol(8) and $\Delta^{3:8(9)}$ -*m*-menthadiene:



in quantity sufficient to allow of their physical properties being determined with accuracy. During the course of these experiments, it occurred to us that it would be interesting to attempt the resolution of *dl*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid, and then, with the aid of the active acids, to synthesise and study the physical properties of the corresponding active menthenols and menthadienes. With this object in view, we prepared nearly 200 grams of the inactive acid, and instituted a large number of comparative experiments with alkaloids and other active bases, in the hope of discovering some salt by means of which resolution might be easily and rapidly effected. Owing probably to the very feeble acidic properties of the acid, very few of its salts crystallise, and the only salts which we could obtain which were at all suitable for fractional crystallisation were those with brucine and *l*-menthylamine. In our first experiments, we mixed the sodium salt of the acid (1 mol.) with brucine (1 mol.) and the free acid (1 mol.) (compare Pope and Peachey, Trans., 1899, **75**, 1066), and obtained a brucine salt, which, when decomposed by sodium carbonate, yielded an acid the rotation of which was only $[\alpha]_D + 5.0^\circ$.

The crystalline salt which separates under these conditions is, therefore, in the main, the brucine salt of the *d*-acid.

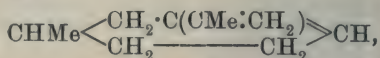
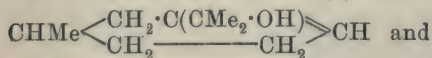
We now treated the acid of $[\alpha]_D + 5.0^\circ$ twice again with brucine under the same conditions, and found that the resulting acid had $[\alpha]_D + 14.5^\circ$. Further experiments in the same direction produced only a very gradual rise in rotatory power, and it was soon evident that very large quantities of material would be required in order to effect complete resolution in this way.

After a series of experiments with *l*-menthylamine, the course which was ultimately adopted was to obtain, by the brucine process, as much of the acid of rotatory power $[\alpha]_D + 14.5^\circ$ as possible, and then to continue the resolution with the aid of *l*-menthylamine.

At the same time, a considerable quantity of the *dl*-acid was worked up from the commencement as *l*-menthylamine salt, and the details of these experiments are briefly described in the experimental part of this paper. When the sodium salt of the acid is mixed with *l*-menthylamine hydrochloride, a very sparingly soluble salt is obtained, which, in the main, is the salt of the *d*-acid, but the separation of this salt into its constituents by fractional crystallisation is a most tedious process. The difficulty is apparently of the same kind as that observed in the case of the resolution of *dl*-1-methylcyclohexylidene-4-acetic acid (Perkin, Pope, and Wallach, *Trans.*, 1909, **95**, 1794), and to a less extent in the resolution of *dl*-1-methyl- Δ^5 -cyclohexene-3-carboxylic acid (Perkin, *Trans.*, 1910, **97**, 2140), and appears to be due to the two constituents of the salt separating from solvents in isomorphous mixtures or mixed crystals. When the *l*-menthylamine salt is crystallised from methyl ethyl ketone, it is easy, in two or three operations, to isolate from the mother liquors small quantities of the *laevo*-acid of the comparatively high rotatory power $[\alpha]_D - 30^\circ$, but the separation of the pure salt of the *d*-acid proved to be a very difficult matter, and was only partly possible after a large number of fractional crystallisations carried out under the special conditions described on p. 521. Ultimately, however, after several months' work, we succeeded in isolating, on the one hand, an *l*-menthylamine salt of rotatory power $[\alpha]_D + 5.9^\circ$, which yielded, on treatment with sodium carbonate, *d*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid of rotation $[\alpha]_D + 40.1^\circ$. On the other hand, the systematic treatment of the acid, $[\alpha]_D - 30^\circ$, with brucine and *l*-menthylamine resulted in the separation of *l*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid, which was, however, not quite free from the *d*-isomeride, since the highest rotation recorded was $[\alpha]_D - 35.8^\circ$.

There is not sufficient evidence that the value 40.1° represents the maximum rotation of the active acids, and, indeed, it is very doubtful whether this is the case (compare p. 527), but we were unable to raise the rotation by further fractional crystallisation.

The difficulty of the separation of the *d*- and *l*-isomerides may be gauged by the fact that, although we started with nearly 200 grams of the externally compensated acid, and every precaution was taken to avoid loss, we were only able to isolate 13 grams of the *d*-acid and 15 grams of the *l*-acid with the rotations given above. These acids were converted into the esters, and then, by the action of magnesium methyl iodide and subsequent elimination of water, into *d*- and *l*- Δ^3 -*m*-menthenol(8) and *d*- and *l*- $\Delta^{3:8(9)}$ -*m*-menthadiene:

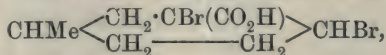


and the observed rotations of the two series may be conveniently tabulated:

	<i>d</i> -Series, [α] _D .	<i>l</i> -Series. [α] _D .
<i>l</i> -Menthylamine salt	+ 5.9°	—
1-Methyl- Δ^3 -cyclohexene-3-carboxylic acid	40.1	— 35.8°
Ethyl methylcyclohexenecarboxylate	32.5	28.9
Δ^3 - <i>m</i> -Menthenol(8)	20.9	18.5
$\Delta^{3:8(9)}$ - <i>m</i> -Menthadiene	17.5	12.9

The low values for the menthadienes are probably due to racemisation during their formation from the menthenols by boiling with 5 per cent. oxalic acid. In order to test this, some ethyl *l*-1-methyl- Δ^3 -cyclohexene-3-carboxylate having [α]_D — 23.5° was converted into Δ^3 -*m*-menthenol(8), and then digested for twelve hours with 10 per cent. oxalic acid. The menthadiene obtained was quite inactive, but no other intramolecular change appeared to have taken place, since this terpene had physical constants almost identical with those of a pure specimen of *dl*- $\Delta^{3:8(9)}$ -*m*-menthadiene (Trans., 1910, 97, 2154), namely, b. p. 177—178°/730 mm., and *n*_D 1.4991.

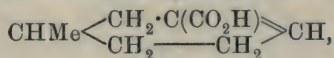
During the course of this research, some of the *d*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid of rotation [α]_D + 40.1° was converted into *d*-3:4-dibromo-1-methylcyclohexan-3-carboxylic acid:



by the action of bromine.

This dibromo-acid was found to melt at 164—165°, and to have [α]_D + 28.5°. The corresponding inactive dibromo-acid melts at 165° (Trans., 1910, 97, 2152).

EXPERIMENTAL.

Resolution of dl-1-Methyl- Δ^3 -cyclohexene-3-carboxylic Acid,

I. *Experiments with Brucine*.—In each experiment, the pure acid (12.5 grams) was suspended in boiling water (750 c.c.), and exactly neutralised with sodium carbonate, a hot concentrated alcoholic solution of the acid (12.5 grams) and brucine (52.5 grams) was then added, and then the whole evaporated on the steam-bath, with frequent additions of small quantities of water, until the alcohol had been removed. During this operation, crystals began to separate, and, on cooling, a large crop of brucine salt was obtained, which was collected, washed with water, and decomposed by sodium carbonate. The crystalline acid was collected, and found to have the following rotation: 0.6395 , made up to 20 c.c. with ethyl acetate, gave, in a 2-dm. tube, $\alpha + 0.32^\circ$, whence $[\alpha]_D + 5.0^\circ$.

This acid was twice submitted to exactly the same process, and the product then had $[\alpha]_D + 14.5^\circ$. The mother liquor from the third treatment was acidified, and, after the acid had been distilled in steam, it had $[\alpha]_D - 9.5^\circ$.

II. *Experiments with l-Menthylamine*.^{*}—When 120 grams of the inactive acid had been resolved to the extent just mentioned, experiments were made with the object of determining whether the separation might not be hastened by using some other active base. After several alkaloids had been tried without success, it was found that the salts with *l*-menthylamine were very sparingly soluble, and crystallised very readily. Unfortunately, owing probably to the formation of isomorphous mixtures, the separation of the isomeric salts proved to be exceedingly tedious, and, as the whole process of separation cannot be given, the following examples will sufficiently illustrate the extent to which separation takes place in the most favourable cases.

(A) The *dl*-acid (10 grams) was dissolved in *N*-sodium hydroxide (70 c.c.) and water (150 c.c.), and, after heating to boiling, a quantity of *l*-menthylamine hydrochloride (7 grams), sufficient to combine with half the acid, was rapidly run in, when the salt separated at once as a crystalline mass, and was collected and dried on porous porcelain. The acid obtained by acidifying the filtrate had a rotation of $[\alpha]_D - 3.4^\circ$, and, after the menthylamine salt had been twice crystallised from ethyl acetate (in which it is sparingly

^{*} The *l*-menthylamine hydrochloride used in all these experiments had $[\alpha]_D - 35.4^\circ$.

soluble in the cold, but readily so on boiling), and decomposed by sodium carbonate, the acid had $[\alpha]_D + 9.0^\circ$

(B) A specimen of the acid, which had $[\alpha]_D + 9.5^\circ$ (60 grams), was dissolved in *N*-sodium hydroxide (420 c.c.), and mixed with excess of *l*-menthylamine hydrochloride (90 grams). The salt which separated was collected, dried on porous porcelain, and crystallised three times from ethyl acetate, when it exhibited the following rotation:

0.7117, made up to 20 c.c. with ethyl alcohol, gave, in a 2-dcm. tube, $\alpha - 1.28^\circ$, whence $[\alpha]_D - 18^\circ$.

The mother liquor was evaporated to a small bulk, and the salt, which separated on cooling, was collected, and the filtrate decomposed with sodium carbonate, when a small quantity of acid (5 grams) was obtained, which, after steam distillation, had $[\alpha]_D - 10^\circ$. A considerable quantity of the acid of $[\alpha]_D - 10^\circ$ which had accumulated (60 grams) was dissolved in *N*-sodium hydroxide (420 c.c.), treated with excess of *l*-menthylamine hydrochloride (90 grams), and the salt recrystallised from the least possible quantity of methyl ethyl ketone. After collection the filtrate yielded, on treatment with sodium carbonate and steam distillation in the usual way, 4 grams of an acid, which had $[\alpha]_D - 30^\circ$.

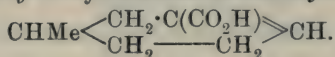
(C) The acid of rotation $[\alpha]_D + 14.5^\circ$, which had been obtained as the result of the partial resolution with brucine, was dissolved, in quantities of 16 grams, in *N*-sodium hydroxide (112 c.c.), and mixed with *l*-menthylamine hydrochloride (25 grams). The salt was collected, dissolved in boiling methyl ethyl ketone, and, when the whole had cooled to 40° , the crystalline mass was rapidly collected. After this operation had been repeated six times, 8 grams of the *l*-menthylamine salt of the *d*-acid resulted: 0.6012, made up to 20 c.c. with alcohol, gave, in a 2-dcm. tube, $\alpha + 0.36^\circ$, whence $[\alpha]_D + 5.9^\circ$.

On further recrystallisation, the rotation of this salt did not alter; it is therefore possibly free from the salt of the *l*-acid.

As has already been stated, it is a comparatively easy matter to isolate small quantities of the *l*-acid of rotation $[\alpha]_D - 30^\circ$ (see B), but the purification of the salt of the *d*-acid is always very tedious. The best way of effecting this seems to be to dissolve the salt in a considerable quantity of a boiling mixture of 90 parts of methyl ethyl ketone and 10 parts of alcohol, and then to shake well in a corked flask until the whole has cooled to 45° , and filter rapidly by the aid of the pump. This process is repeated with the crop of crystals which separates from the mother liquor until the bulk of the *l*-salt has been removed. The large quantities of mother liquor which will have accumulated are then concentrated considerably,

and, after the salt has crystallised out, the filtrate is decomposed with sodium carbonate, and the crude, rather brown *l*-acid purified by distillation in steam. By repeating these processes many times, separation of the *d*- and *l*-isomerides is ultimately accomplished.

d-1-Methyl- Δ^3 -cyclohexene-3-carboxylic Acid,



The *l*-menthylamine salt of this acid, obtained as described on p. 522, has $[\alpha]_D + 5.9^\circ$, melts at about $150\text{--}152^\circ$, and is readily soluble in alcohol and in boiling ethyl acetate or methyl ethyl ketone, but very sparingly so in these two solvents in the cold. The acid, obtained from the salt by decomposition with sodium carbonate, was distilled in steam and left in contact with porous porcelain until dry; it then melted at $62\text{--}64^\circ$ (the *dl*-acid melts at 58°):

0.1164 gave 0.2928 CO_2 and 0.0914 H_2O . $\text{C} = 68.7$; $\text{H} = 8.7$.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires $\text{C} = 68.6$; $\text{H} = 8.6$ per cent.

0.5218, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 2.09^\circ$, whence $[\alpha]_D + 40.1^\circ$.

Ethyl d-1-Methyl- Δ^3 -cyclohexene-3-carboxylate.—This ester was prepared by digesting the acid (12 grams) with 100 c.c. of 10 per cent. alcoholic sulphuric acid for two hours on the steam-bath; the product was then diluted with water, and extracted with ether.

The ethereal solution was thoroughly washed with dilute sodium carbonate, dried, evaporated, and the ester distilled, when it passed over constantly at $150\text{--}151^\circ/100$ mm. 0.6148, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 2.0^\circ$, whence $[\alpha]_D + 32.5^\circ$.

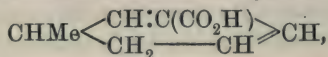
d-3: 4-Dibromo-1-methylcyclohexan-3-carboxylic Acid (compare p. 520).—In preparing this dibromo-acid, the pure *d*-acid (1 gram), dissolved in chloroform (5 c.c.) and cooled to -10° , was mixed with a slight excess of bromine (1.2 grams), and, after remaining in the freezing mixture for one hour, it was kept at the ordinary temperature for two hours, during which a quantity of solid separated. The chloroform was allowed to evaporate, the residue left in contact with porous porcelain until quite dry, and then re-crystallised from formic acid, in which it is sparingly soluble, and from which it separates in colourless leaflets, melting at 165° , at which temperature the *dl*-dibromo-acid also melts:

0.2848 gave 0.3567 AgBr. $\text{Br} = 53.2$.

$\text{C}_8\text{H}_{12}\text{O}_2\text{Br}_2$ requires $\text{Br} = 53.3$ per cent.

0.6202, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 1.77^\circ$, whence $[\alpha]_D + 28.5^\circ$.

A curious result was obtained in an attempt to study what change in optical activity would result if the dihydro-acid:



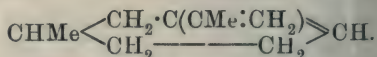
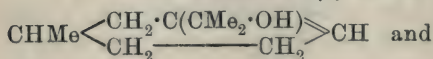
could be prepared from the active dibromo-acid by the elimination of two molecules of hydrogen bromide. A considerable quantity (14 grams) of an acid which had $[\alpha]_D + 17.4^\circ$ was converted into the ester; this was dissolved in pure ether, cooled to -10° , and mixed with the quantity of bromine calculated for the formation of the dibromo-additive compound, a quantity which was rapidly absorbed.

The ether was then distilled off under slightly diminished pressure, and the residue added to a concentrated and boiling solution of potassium hydroxide (30 grams) in methyl alcohol, when a vigorous action took place and potassium bromide was immediately precipitated. The product, diluted with water, was nearly neutralised with hydrochloric acid, evaporated, and mixed with excess of acid, when a syrup separated, which soon crystallised. The acid was collected, washed, and separated into four portions by fractional distillation in steam, but in each case, after collecting and draining on porous porcelain, the acid melted at $60-62^\circ$, and consisted of 1-methyl- Δ^3 -cyclohexene-3-carboxylic acid, since, when mixed with this acid, there was no alteration in melting point. The identity was also confirmed by analysis. (Found, C=68.5; H=8.8. Calc., C=68.6; H=8.8 per cent.)

The different portions of the acid were mixed, and the rotation determined.

1.1197, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 1.95^\circ$, whence $[\alpha]_D + 17.4^\circ$, and therefore no change in rotation had occurred during the course of the above somewhat drastic experiments. Since almost the whole of the acid was recovered, it is obvious that when ethyl 3:4-dibromo-1-methylcyclohexan-3-carboxylate is digested with methyl-alcoholic potassium hydroxide, the alkali acts simply as an agent for removing bromine.

d- Δ^3 -*m*-Menthenol(8) and $\Delta^{3:8(9)}$ -*m*-Menthadiene,



The synthesis of *d*- Δ^3 -*m*-menthenol(8) was carried out by adding ethyl *d*-1-methyl- Δ^3 -cyclohexene-3-carboxylate (12 grams) to an ethereal solution of magnesium methyl iodide prepared from 6 grams of magnesium, and, after remaining overnight, the product was decomposed by water and distilled in steam. The distillate was

extracted with ether, the ethereal solution dried and fractionated, when *d*- Δ^3 -*m*-menthenol(8) passed over constantly at 107—108°/25 mm. as a viscid syrup, which exhibited the following properties: *d* 20/20° 0.9235, n_D 1.4791, *M* 47.3 (calc., 47.16). 0.7231, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 1.51^\circ$, whence $[\alpha]_D + 20.9^\circ$.

These properties agree closely with those of *dl*- Δ^3 -*m*-menthenol(8) (Trans., 1910, 97, 2158), which has b. p. 102°/14 mm., *d* 20/20° 0.9268, n_D 1.4798.

In order to obtain $\Delta^{3:8(9)}$ -*m*-menthadiene, the menthenol was digested for four hours with 5 per cent. oxalic acid, and the product distilled in steam. After extraction with ether, and distillation first alone, and then twice over sodium, the terpene distilled constantly at 179°/730 mm., and had n_D 1.4972, whereas *dl*- $\Delta^{3:8(9)}$ -*m*-menthadiene (*loc. cit.*, p. 2154) distilled at 181—182°/760 mm., and had n_D 1.4975.

0.7117, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 1.25^\circ$, whence $[\alpha]_D + 17.5^\circ$.

l-1-Methyl- Δ^3 -cyclohexene-3-carboxylic Acid, *l*- Δ^3 -*m*-Menthenol(8),
and *l*- $\Delta^{3:8(9)}$ -*m*-Menthadiene.

In experiment (C) on p. 522, a method is described by which *l*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid may be comparatively easily obtained with the rotation $[\alpha]_D - 30^\circ$, and, when a considerable quantity of this acid had accumulated, it was again converted into the *l*-menthylamine salt, and, after a long series of fractional crystallisations, an acid (15 grams) was obtained, which exhibited the following rotation: 0.7447, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha - 2.67^\circ$, whence $[\alpha]_D - 35.8^\circ$. No doubt, if this acid had again been converted into the *l*-menthylamine salt, and the fractional crystallisation continued, an acid of somewhat higher rotation would have been obtained, but the loss which this must have entailed would have been serious.

Ethyl l-1-methyl- Δ^3 -cyclohexene-3-carboxylate, prepared from the acid by means of alcoholic sulphuric acid, exactly as described in the case of the corresponding *d*-ester (p. 523), distilled at 148—150°/100 mm. 0.8239, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha - 2.38^\circ$, whence $[\alpha]_D - 28.9^\circ$.

l- Δ^3 -*m*-Menthenol(8) was obtained from this ester (11 grams) by treatment with magnesium methyl iodide (*Mg*=5 grams) in the usual way, and, after distillation in steam, distilled constantly at 102—103°/14 mm. 0.8111, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha - 1.50^\circ$, whence $[\alpha]_D - 18.5^\circ$. This menthenol was digested with 5 per cent. oxalic acid for two hours,

and, after distillation in steam, and then three times over sodium, *l*- $\Delta^{3:8(9)}$ -*m*-menthadiene boiled constantly at 181—182°/760 mm. 0.8118, made up 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha - 1.05^\circ$, whence $[\alpha]_D - 12.9^\circ$.

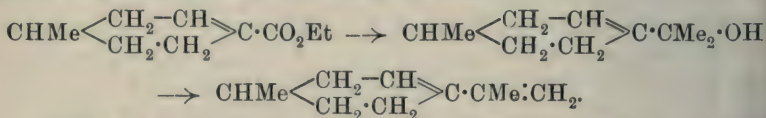
This determination of the refractive index gave $n_D 1.4969$.

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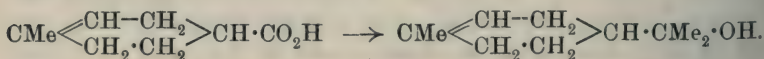
LXII.—Experiments on the Synthesis of the Terpenes. Part XVII. *d*- Δ^3 -*p*-Menthenol(8) and *d*- $\Delta^{3:8(9)}$ -*p*-Menthadiene.

By TSAN QUO CHOU and WILLIAM HENRY PERKIN, jun.

THE externally compensated modifications of Δ^3 -*p*-menthenol(8) and $\Delta^{3:8(9)}$ -*p*-menthadiene were first prepared in 1905 (Perkin and Pickles, *Trans.*, **87**, 647) from the ester of *dl*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid by treatment with magnesium methyl iodide and subsequent elimination of water:



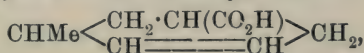
Shortly afterwards, Kay and Perkin (*Trans.*, 1906, **89**, 839) resolved *dl*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid by means of the brucine salt into the *d*- and *l*-acids, which were obtained with rotations $[\alpha]_D + 101.1^\circ$ and -100.8° respectively. From these active acids the *d*- and *l*-modifications of Δ^3 -*p*-menthenol(8) and $\Delta^{3:8(9)}$ -*p*-menthadiene were prepared, and the rotations of all these substances are tabulated on p. 529. During the progress of these experiments on the synthesis of the terpenes, other attempts were made to prepare active menthenols and menthadienes by processes similar to that just mentioned. Thus, in 1908, Fisher and Perkin (*Trans.*, **93**, 1871) resolved *dl*-1-methyl- Δ^1 -cyclohexene-4-carboxylic acid into the *d*- and *l*-acids of rotations $[\alpha]_D + 50^\circ$ and -52° respectively, and prepared from these the *d*- and *l*-modifications of terpineol which were obtained with the rotations $[\alpha]_D + 44.2^\circ$ and -46.6° :



The attempt to convert these active terpineols into the pure active

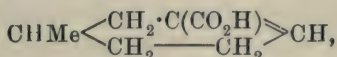
limonenes was not successful, since, even when the elimination of water was carried out at the ordinary temperature with the aid of magnesium methyl iodide, the resulting limonene had a rotation of only 5° .

Shortly afterwards (Perkin, Trans., 1910, **97**, 2131), the resolution of *dl*-1-methyl- Δ^5 -cyclohexene-3-carboxylic acid:



was attempted with the aid of *l*-menthylamine as the active base, and the *d*- and *l*-acids were obtained with the rotations $[\alpha]_D + 33.1^\circ$ and -30.9° respectively. These yielded, on treatment with magnesium methyl iodide and subsequent elimination of water, Δ^5 -*m*-menthenol(8) and $\Delta^{5:8(9)}$ -*m*-menthadiene, which, in the *d*-series, had $[\alpha]_D + 36.7^\circ$ and $+29.6^\circ$ respectively.

In the paper directly preceding the present communication (p. 521), experiments on the resolution of *dl*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid:



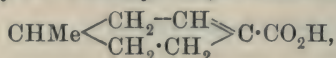
are described, and it is there shown that this acid may be resolved with the aid of *l*-menthylamine into the *d*- and *l*-modifications with the rotations $[\alpha]_D + 40.1^\circ$ and -35.8° respectively, and these were converted, by the usual methods, into the corresponding *d*- and *l*-menthenols and menthadienes, of which the highest rotations observed, in the *d*-series, were $[\alpha]_D + 20.9^\circ$ and $+17.5^\circ$ respectively. In all these cases, separation of the optically active acids from the externally compensated modifications has always been a long and tedious process, and there appears to be no doubt that this is largely, if not wholly, due to the isomeric salts separating from solvents as isomorphous mixtures or mixed crystals, which are only very gradually resolvable by further fractional crystallisation. This difficulty might conceivably be got over if the active base employed for the separation could be varied, but the cyclohexenecarboxylic acids are, unfortunately, so feebly acidic that very few of their salts with active bases are sufficiently stable or well characterised to make them suitable for fractional crystallisation.

When the available data are carefully considered, it is difficult to avoid the conclusion that, in the cases detailed above, separation may have, after all, been incomplete. The salts of the active acids were probably still partly racemic, and in the form of mixed crystals, and, for these reasons, separation by further fractional crystallisation was practically impossible, at all events with the comparatively small amounts of material which were available.

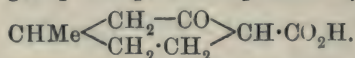
Confirmatory evidence of this is afforded by the experiments of

Fisher and Perkin on the resolution of *dl*-1-methyl- Δ^1 -cyclohexene-3-carboxylic acid (see p. 526). The value observed for the *l*-acid was $[\alpha]_D -52^\circ$, and that this is probably not the maximum value is indicated by the fact that the *l*-terpineol obtained from this acid had only $[\alpha]_D -46.6^\circ$, whereas an *l*-terpineol has been obtained from pinene with $[\alpha]_D -117.5^\circ$ (Ertschikowsky, *Ber.*, 1896, **29**, 887).

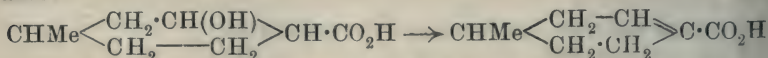
Considerations such as these made it desirable that the actual extent of the resolution effected by the fractional crystallisation of the salts of the cyclohexene acids with active bases should, at least in one instance, be experimentally tested, and we have therefore carried out an interesting series of experiments in connexion with the optical activity of 1-methyl- Δ^3 -cyclohexene-4-carboxylic acid:



which have a direct bearing on this problem. In a communication recently published (Gardner, Perkin, and Watson, *Trans.*, 1910, **97**, 1759, 1767), it was shown that *d*-1-methylcyclohexan-3-one (from pulegone, $[\alpha]_D + 8.8^\circ$) is converted, by the action of sodamide and carbon dioxide, into a carboxylic acid, in which it was assumed that the carboxyl group occupied the position (4):



That this acid, which has $[\alpha]_D + 97.2^\circ$, is, in fact, *d*-1-methylcyclohexan-3-one-4-carboxylic acid has now been proved in the following way. When this keto-acid is reduced with sodium amalgam, it is converted into *d*-1-methylcyclohexan-3-ol-4-carboxylic acid, which has $[\alpha]_D - 31.8^\circ$, and this, on treatment with sulphuric acid at $85-90^\circ$, yields *p*-toluic acid, a proof that the carboxylic group in the hexanol acid occupies the position (4) in relation to the methyl group. The elimination of water from *d*-1-methylcyclohexan-3-ol-4-carboxylic acid takes place with difficulty, but it may be accomplished (p. 533) with the aid of phosphorus trichloride, and the resulting *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid:



was found to have $[\alpha]_D + 150.1^\circ$. This acid was converted into the corresponding *d*- Δ^3 -*p*-menthenol(8) and $\Delta^{3:8(9)}$ -*p*-menthadiene by the usual methods, and the $[\alpha]_D$ values observed (I) may be conveniently tabulated in comparison with those previously observed by Kay and Perkin (II) (*loc. cit.*):

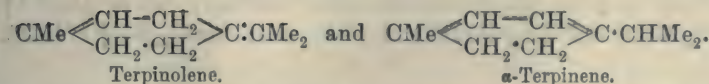
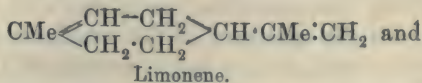
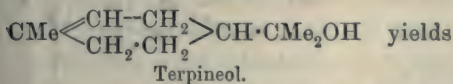
	I.	II.
<i>d</i> -1-Methyl- Δ^3 -cyclohexene-4-carboxylic acid	+150.1°	+101.1°
Ethyl <i>d</i> -1-methylcyclohexenecarboxylate	122.3	86.5
<i>d</i> - Δ^3 - <i>p</i> -Menthenol(8).....	83.2	67.3
<i>d</i> - $\Delta^{3:8(9)}$ - <i>p</i> -Menthadiene.....	100.0	98.2

This table shows quite clearly that the substances obtained by Kay and Perkin had rotations which were only about two-thirds of the maximum value. There is, however, one curious exception to this, and that is the case of the menthadienes, which, although derived from menthenols of the widely different values as $[\alpha]_D + 83.2^\circ$ and $+67.3^\circ$, had, in both cases, practically the same rotations, namely, $+100.0^\circ$ and $+98.2^\circ$. This seems to indicate quite clearly that some racemisation must have taken place in any case during the formation of the menthadiene from the menthenol of rotation $[\alpha]_D + 83.2^\circ$.

That racemisation does undoubtedly take place under certain conditions, to some extent at least, is proved by the following experiment.

Pure *d*- Δ^3 -*p*-menthenol(8) of rotation $[\alpha]_D + 83.2^\circ$ was converted into *d*- $\Delta^{3:8(9)}$ -*p*-menthadiene by two different processes, namely, (i) by digesting with 5 per cent. oxalic acid, and (ii) by the action of magnesium methyl iodide in the cold. The menthadiene obtained in (i) had $[\alpha]_D + 100.0^\circ$, whereas the preparation resulting from (ii) had a rotation of $[\alpha]_D + 90.4^\circ$ only. Racemisation in unsaturated compounds is usually assumed to be due to the reversible migration of the double linking, with consequent loss of optical activity, and seems to have been observed previously only in cases where the double linking is closely associated with the asymmetric carbon atom.

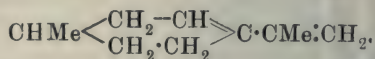
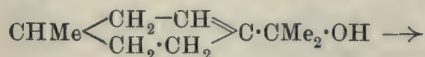
Thus, for example, Wallach has shown that terpineol yields, on treatment with dehydrating agents, not only limonene, but also terpinolene and α -terpinene:



This group of terpenes probably represents an equilibrium mixture, but, however that may be, it is quite clear that, if the terpineol in the first instance is optically active, the reversible change into terpinolene alone must ultimately result in the inactivity of the

whole. This migration of the double linking with consequent loss of optical activity accounts therefore in a satisfactory manner for the fact that Fisher and Perkin (*loc. cit.*) were unable to obtain an active limonene with a rotation of more than 5° (*d*-limonene has $[\alpha]_D +105^\circ$) from active terpineol by the elimination of water.

It is, however, difficult to understand how this explanation of loss of activity can be applied to the case of racemisation during the elimination of water from *d*- Δ^3 -*p*-menthenol(8):

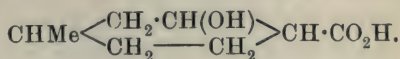
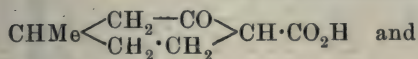


since migration of the double linking could hardly affect the asymmetric grouping $\gg \text{CHMe}$ to which optical activity is due unless, indeed, some profound change in constitution is assumed to take place.

Moreover, it is clear that a profound change in constitution does not take place, because the menthadiene obtained is found to exhibit all those physical properties which are known to be associated with the presence of the conjugated double linking.

Note by W. H. Perkin.—The paper by Kay and Perkin already referred to (Trans., 1906, **89**, 850; compare *ibid.*, 1905, **87**, 639) contains a description of some of the physical properties of *dl*- $\Delta^{3:8(9)}$ -*p*-menthadiene, which subsequent investigation has shown to be incorrect, and which has resulted in some confusion (compare Perkin and Wallach, Trans., 1910, **97**, 1437). As this terpene was very carefully prepared from crystalline *dl*- Δ^3 -*p*-menthenol(8), and had the correct boiling point (184 — 185°), it was difficult to understand the inaccuracy of the density and refraction values. The reason has now been ascertained to be the following one. The terpene was obtained in rather small quantity, and was washed into the bottle with a little ether and sent to Sudbury for investigation, the intention being that the final distillation should be carried out just before the physical constants were determined. This was, however, not done, and the determinations were made with the specimen in the condition in which it was received. The specimen has now been re-examined, and, after twice distilling over sodium, it gave the following correct values: b. p. 184 — 185° ; $d_{20/20^\circ}$ 0.8598 ; n_D 1.4919 ; M 45.9 . Calc. for $\text{C}_{10}\text{H}_{16}$ F^2 45.24 .

d-1-Methylcyclohexan-3-one-4-carboxylic Acid and *d*-1-Methylcyclohexan-3-ol-4-carboxylic Acid,



d-1-Methylcyclohexan-3-one-4-carboxylic acid had already been prepared in small quantities by Gardner, Perkin, and Watson (Trans., 1910, 97, 1767) from *d*-1-methylcyclohexan-3-one (from pulegone) by the action of sodamide and carbon dioxide at the ordinary temperature on its solution in light petroleum, but the yield obtained at that time was very unsatisfactory. As it was necessary to obtain a large quantity of this acid for the experiments described in the present communication, we made a number of comparative experiments, and succeeded in working out the following method of preparation, which gives excellent results. *d*-1-Methylcyclohexan-3-one (from Schimmel, $[\alpha]_D + 8.8^\circ$), in quantities of 100 grams, is dissolved in one and a-quarter litres of light petroleum (b. p. $50-60^\circ$) in a three-necked flask fitted with a reflux condenser and mechanical stirrer, and the whole heated to boiling on the steam-bath. The steam is then turned off, the stirrer set in motion, and powdered sodamide (40 grams) added in several portions during twenty minutes, when a rapid evolution of ammonia takes place. A rapid current of carefully dried carbon dioxide is now passed, when reaction readily occurs with sufficient rise of temperature to keep the light petroleum boiling, and, in a short time, a quantity of the sodium salt of the ketonic acid separates. As soon as the liquid ceases to boil, the steam is turned on again, and the passage of the carbon dioxide continued for three and a-half hours; the contents of the flask are allowed to cool, and washed into a separating funnel with sufficient ice water to dissolve all the sodium salt. The aqueous layer is separated, filtered, if necessary, and acidified with ice-cold dilute hydrochloric acid, when the ketonic acid separates as a crystalline mass, which is collected and drained on porous porcelain. The yield of air-dry acid is usually about 70 grams, but on more than one occasion 90 grams have been obtained; in this condition it is pure enough for conversion into the hydroxy-acid (see below). The pure keto-acid is obtained from this product by dissolving in ether, extracting with sodium carbonate, and cautiously adding dilute hydrochloric acid to the alkaline solution until traces of yellow impurity have been precipitated. After filtering, the filtrate deposits, on acidifying, pure *d*-1-methylcyclohexan-3-one-4-carboxylic acid as a colourless, crystalline mass. The petroleum layer,

separated from the sodium salt of the acid in the manner described above, yields, on evaporation, a good deal of unchanged ketone, which is readily purified by distillation in steam.

d-1-Methylcyclohexan-3-ol-4-carboxylic Acid.—In preparing this acid, *d*-1-methylcyclohexan-3-one-4-carboxylic acid (15 grams) is dissolved in sodium carbonate, diluted to one litre with hot water (50°), and reduced in a wide-necked bottle with one kilo. of freshly prepared sodium amalgam (3 per cent.), which is added all at once.

During the operation, which takes about three hours, a rapid current of carbon dioxide is passed, the whole is vigorously stirred by a mechanical stirrer, and the temperature gradually raised to 70° by circulating a stream of hot water round the bottle. After remaining overnight, the aqueous liquor is decanted from the mercury, acidified with hydrochloric acid, and distilled in steam.

By this means, unchanged keto-acid, which is always present, is decomposed, the ketone passes over and is recovered from the distillate. The liquid in the steam distillation flask is evaporated on the steam-bath until a pale yellow oil commences to separate; it is then saturated with salt, and extracted three times with ether.

After drying over anhydrous sodium sulphate, and evaporating, the ethereal solution deposits a viscid syrup, which gradually becomes semi-solid; it distils at 185—190°/22 mm., but with some decomposition, and the distillate has $[\alpha]_D$ about -7.5° (compare p. 528). This doubtless consists of a mixture of the *cis*- and *trans*-modifications of *d*-1-methylcyclohexan-3-ol-4-carboxylic acid.

The best way to purify this hydroxy-acid is with the aid of its ethyl ester, which is readily prepared by digesting on the steam-bath with a large excess of 10 per cent. alcoholic sulphuric acid for two to three hours. The ester is isolated by diluting with water and extracting with ether in the usual manner, the ethereal solution washed with sodium carbonate, dried, evaporated, and the residue fractionated, when almost the whole quantity passes over at 135°/20 mm.:

0.1679 gave 0.3961 CO₂ and 0.1484 H₂O. C=64.4; H=9.8.

C₁₀H₁₈O₃ requires C=64.5; H=9.7 per cent.

d 20/20° 1.026; n_D 1.458; M 49.25 (calc., 49.51). 1.0221, made up to 20 c.c., with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 0.6^\circ$, whence $[\alpha]_D + 5.9^\circ$.

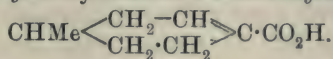
Conversion of d-1-Methylcyclohexan-3-ol-4-carboxylic Acid into *p*-Toluic Acid.—The hydroxy-acid employed in this experiment was the crystalline modification obtained by leaving the semi-solid mixture direct from the reduction of the keto-acid in contact with porous porcelain. This acid dissolves readily in concentrated sulphuric acid, and, when the colourless solution is heated at

85—90°, evolution of sulphur dioxide occurs freely with very little darkening.

After a few minutes, the hot solution is diluted with water, the crystalline precipitate collected, washed well, dissolved in dilute sodium carbonate, and digested with animal charcoal. Finally the acid is again precipitated and crystallised from dilute acetic acid. (Found, C=70·5; H=6·0. Calc., C=70·6; H=5·9 per cent.)

This acid separated from dilute acetic acid in colourless, glistening needles, melted at 177—178°, and had all the properties of *p*-toluic acid. The identity was further proved by mixing it with a specimen of pure *p*-toluic acid, when there was no alteration in the melting point.

d-1-Methyl- Δ^3 -cyclohexene-4-carboxylic Acid,



The conversion of *d*-1-methylcyclohexan-3-ol-4-carboxylic acid into *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid by the elimination of water does not take place very readily, but digesting the hydroxy-acid with acetyl chloride containing phosphorus trichloride, and distilling the product first under diminished pressure and then in steam, yields small quantities of the unsaturated acid. Other dehydrating agents give a similar result, but the best yield is apparently produced under the following conditions. Ethyl *d*-1-methylcyclohexan-3-ol-4-carboxylate, in quantities of 10 grams, is digested on the water-bath with an equal weight of phosphorus trichloride for one hour, and then heated to boiling on the sand-bath for half an hour.

The orange-coloured product is poured into excess of alcohol, and, after two hours, water is added, the ester extracted with ether, the ethereal solution washed with sodium carbonate, dried, evaporated, and the residue distilled, when crude ethyl *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylate passes over at 148—150°/100 mm., the yield being about 60 to 70 per cent. of that theoretically possible. The ester is hydrolysed by digesting with excess of methyl-alcoholic potassium hydroxide, and, after diluting with water, evaporating until free from methyl alcohol and acidifying, the semi-solid precipitate is collected and distilled in a current of steam. The unsaturated acid passes over with some difficulty, but in a pure condition, and is collected and left in contact with porous porcelain until dry. From the aqueous filtrate, a further considerable quantity of acid is recovered by neutralising, evaporating to a small bulk, and acidifying:

0·1101 gave 0·2760 CO₂ and 0·0849 H₂O. H=68·5; H=8·6.

C₈H₁₂O₂ requires C=68·6; H=8·6 per cent.

1.007, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 15.02^\circ$, whence $[\alpha]_D + 150.1^\circ$. *d*-1-Methyl- Δ^3 -cyclohexene-4-carboxylic acid is very sparingly soluble in water, but the hot concentrated solution deposits the acid as a chalky powder, which, under the microscope, is seen to consist of well-defined, elongated, four-sided prisms. It melts at $136\text{--}137^\circ$ (the *dl*-acid melts at 134° : Trans., 1905, **87**, 646), and the solution in sodium carbonate reduces permanganate instantly.

Ethyl d-1-Methyl- Δ^3 -cyclohexene-4-carboxylate.—The ester obtained by the action of phosphorus trichloride on ethyl *d*-1-methylcyclohexan-3-ol-4-carboxylate (see above) is far from pure, and usually has a rotation of $[\alpha]_D + 65^\circ$ only; the pure ester is obtained from the pure acid by means of alcohol and sulphuric acid, but esterification takes place with some difficulty, especially in the cold. The acid (18 grams) was left in contact with alcohol (200 c.c.) and sulphuric acid (15 c.c.) for twenty-four hours, and then heated for three hours on the steam-bath. After adding water, the ester was extracted with ether, the ethereal solution washed with sodium carbonate (which extracted 3 grams of unchanged acid), dried, evaporated, and the ester distilled, when it passed over constantly at $151\text{--}152^\circ/100$ mm.:

0.1094 gave 0.2870 CO_2 and 0.0954 H_2O . C = 71.5; H = 9.7.

$\text{C}_{10}\text{H}_{16}\text{O}_2$ requires C = 71.4; H = 9.5 per cent.

d 20/20° 0.9757; n_D 1.4688; M 47.9 (calc., 47.3). 0.9639, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 11.79^\circ$, whence $[\alpha]_D + 122.3^\circ$.

d-3-Bromo-1-methylcyclohexan-4-carboxylic Acid.*—In order to prepare this acid, *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid was mixed with a large excess of fuming hydrobromic acid (saturated at 0°), in which it gradually dissolved, and, after remaining overnight, the product was heated at 80° for one hour and then mixed with three volumes of water. The bromo-acid, which separated as a voluminous, crystalline mass, was collected, washed, and crystallised from formic acid, from which it was deposited, on slow cooling, as a mass of asbestos-like threads, melting at $133\text{--}134^\circ$:

0.1633 gave 0.1395 AgBr. Br = 36.4.

$\text{C}_8\text{H}_{13}\text{O}_2\text{Br}$ requires Br = 36.2 per cent.

1.1866, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 8.50^\circ$, whence $[\alpha]_D + 71.7^\circ$. This bromo-acid dissolves readily in sodium carbonate, and when the solution was boiled, a small quantity of an oil having the odour of a bromo-

* The corresponding *dl*-bromo-acid has already been described (Trans., 1905, **87**, 646), but the melting point was accidentally omitted. It softens at 135° and melts at $140\text{--}142^\circ$.

hydrocarbon separated, and, after this had been removed, the alkaline solution gave, on acidifying, a colourless precipitate of *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid, which melted at 134—136°, and had approximately the same rotation, $[\alpha]_D +150^\circ$, as before the conversion into the bromo-acid.

d-3: 4-Dibromo-1-methylcyclohexan-4-carboxylic Acid.—This dibromo-acid is readily obtained when *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid, dissolved in chloroform and cooled to -10° , is mixed with a chloroform solution of the calculated amount of bromine. Addition takes place slowly in the cold, but if the temperature of the solution is allowed to gradually rise to 17° , the colour of the bromine disappears, and the chloroform solution deposits, on evaporation in the air, a solid residue. After remaining in contact with porous porcelain until dry, the substance was crystallised from formic acid, from which it separated as a colourless, glistening mass of flat needles, melting at about 158° :

0.1591 gave 1.1990 AgBr. Br=53.1.

$C_8H_{12}O_2Br_2$ requires Br=53.3 per cent.

0.9364, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha +9.58^\circ$, whence $[\alpha]_D +102.2^\circ$. This dibromo-acid dissolves readily in sodium carbonate, but the solution, on boiling, does not deposit a bromo-hydrocarbon, as has so often been observed in analogous cases.

Reduction of d-1-Methyl- Δ^3 -cyclohexene-4-carboxylic Acid. *Formation of the cis- and trans-Modifications of 1-Methylcyclohexan-4-carboxylic Acid.*

The reduction of *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid was carried out with colloidal palladium and hydrogen according to the excellent method described by A. Skita (*Ber.*, 1909, **42**, 1630), with the modification that the process was conducted at the ordinary pressure instead of under a pressure of two atmospheres. Gum arabic (5 c.c. of a solution of 25 grams in 100 c.c. of water) was diluted with warm water (200 c.c.), mixed with a solution of the unsaturated acid (15 grams) in alcohol (200 c.c.), and, after cooling to 25° , a solution of palladous chloride (1 gram) in water was added. The solution was transferred to a long, narrow cylinder, and hydrogen passed in for two days; the product was then distilled in steam, when an oil passed over at first, but towards the end of the distillation this crystallised.

The distillate was neutralised with sodium carbonate, evaporated to about 300 c.c. and mixed with powdered ice and a few c.c. of permanganate solution, and allowed to remain for one hour, but

hardly any decoloration of the permanganate took place, showing that reduction was practically complete. After removing the excess of permanganate with sodium sulphite, the acid was liberated by hydrochloric acid and again distilled in steam. The distillate was extracted with ether, the ethereal solution dried, evaporated, and the residual oil fractionated, when almost the whole passed over at $141^{\circ}/20$ mm. as a colourless oil, which, in the ice chest, deposited a quantity of crystals. The product was transferred to porous porcelain, and, when the oil had been absorbed, the residue (2 grams) was crystallised from a little formic acid; it consisted then of pure *trans*-1-methylcyclohexan-4-carboxylic acid:

0.1154 gave 0.2853 CO_2 and 0.1031 H_2O . $\text{C}=67.4$; $\text{H}=9.9$.

$\text{C}_8\text{H}_{14}\text{O}_2$ requires $\text{C}=67.6$; $\text{H}=9.8$ per cent.

This acid melted at 112° , and is obviously identical with the hexahydro-*p*-toluic acid described by Perkin and Pickles (Trans., 1905, **87**, 644). The *p*-toluidide was prepared by warming the acid (1 gram) with phosphorous trichloride (0.5 gram) on the water-bath, and then mixing with an ethereal solution of *p*-toluidine (5 grams). The ethereal solution was washed with water, dried, and evaporated, during which operation the *p*-toluidide, which is rather sparingly soluble in ether, separated in crystals. It is readily soluble in alcohol, and separates from 80 per cent. alcohol as a glistening mass of flat prisms, which melt at 179 — 180° :

0.1482 gave 8.4 c.c. N_2 at 17° and 735 mm. $\text{N}=6.3$.

$\text{C}_{15}\text{H}_{21}\text{ON}$ requires $\text{N}=6.1$ per cent.

The porous plates used in the purification of the *trans*-acid were extracted with ether in a Soxhlet apparatus, and the oily acid boiled with much water and freshly precipitated calcium carbonate.

When the filtered solution was concentrated on the water-bath, a calcium salt separated in long needles; this was found to be the calcium salt of the *trans*-acid, and, on acidifying, 0.7 gram of this acid separated at once in the crystalline form. On further concentration, the mother-liquors of this calcium salt deposited a second crop, which consisted principally of the salt of the *cis*-acid, and, when this and a further crop had been removed, the filtrate yielded, on acidifying, an oily acid which distilled constantly at $140^{\circ}/20$ mm.

After the purification of the calcium salt had been repeated, the *cis*-1-methylcyclohexan-4-carboxylic acid was analysed:

0.1149 gave 0.2827 CO_2 and 0.1034 H_2O . $\text{C}=67.2$; $\text{H}=10.0$.

$\text{C}_8\text{H}_{14}\text{O}_2$ requires $\text{C}=67.6$; $\text{H}=9.8$ per cent.

The *p*-toluidide of this acid was prepared in the way already described in the case of the *trans*-acid. It is more soluble in ether or alcohol than the *p*-toluidide of the *trans*-acid, and separates

from 70 per cent. alcohol in colourless needles, which soften at 135° and melt at $142\text{--}143^{\circ}$:

0.1833 gave 10.3 c.c. N_2 at 15° and 736 mm. $N=6.4$.

$C_{15}H_{21}ON$ requires $N=6.1$ per cent.

So far as could be judged, the product of the reduction of *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid, under the conditions described above, consists of about 75 per cent. of the *cis*- and 25 per cent. of the *trans*-acids.

d- Δ^3 -*p*-Menthenol(8) and *d*- Δ^3 : $8^{(9)}$ -*p*-Menthadiene,



In order to prepare the former of these substances, pure ethyl *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylate (20 grams) was added to an ethereal solution of magnesium methyl iodide (containing 9 grams of magnesium), and, after remaining for twenty-four hours, water was added and the product distilled in steam. The ethereal extract of the distillate was dried, evaporated, and the residue distilled, when almost the whole quantity passed over at $105^{\circ}/20$ mm.:

0.1414 gave 0.4028 CO_2 and 0.1502 H_2O . $C=77.7$; $H=11.8$.

$C_{10}H_{18}O$ requires $C=77.9$; $H=11.7$ per cent.

d 20/20° 0.9236; n_D 1.4783; M 47.2 (calc., 47.2). 0.9099, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 7.57^{\circ}$, whence $[\alpha]_D + 83.2^{\circ}$. *d*- Δ^3 -*p*-Menthenol(8) is a colourless, rather viscid oil, which, even on long keeping in the ice chest, showed no signs of crystallising; it possesses a pungent odour, recalling that of peppermint and cymene.

d- Δ^3 : $8^{(9)}$ -*p*-Menthadiene was first prepared by boiling the pure menthenol (15 grams) with 200 c.c. of 5 per cent. oxalic acid in a reflux apparatus for ten hours with frequent shaking, when elimination of water was practically complete. The product was distilled in steam, the distillate extracted with ether, the ethereal solution dried, evaporated, and the terpene distilled twice alone and then three times over sodium, when it boiled constantly at $184\text{--}185^{\circ}/776$ mm.:

0.1296 gave 0.4183 CO_2 and 0.1356 H_2O . $C=88.0$; $H=11.7$.

$C_{10}H_{16}$ requires $C=88.2$; $H=11.8$ per cent.

The amount available for the density determination was so small that the value obtained must be accepted as approximate only.

d 16/16° 0.8649; n_D 1.4965; M 45.9; calc. for $C_{10}H_{16}$ F^2 45.24. 0.8544, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 8.54^{\circ}$, whence $[\alpha]_D + 100.0^{\circ}$. For reasons stated in the intro-

duction to this paper (p. 529), it seemed probable that racemisation had taken place to some extent during the formation of this terpene from *d*- Δ^3 -*p*-menthenol(8) under the conditions just described, and that the value $[\alpha]_D + 100^\circ$ does not represent the maximum rotation of the terpene. In order to test this supposition, the following experiment was carried out. Pure ethyl *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylate (12 grams) was added to magnesium methyl iodide (containing 7 grams of magnesium), and, after remaining overnight and then warming on the steam-bath for one hour, the product was mixed with water and dilute hydrochloric acid and distilled in steam (compare footnote, Trans., 1910, **97**, 2154). The ethereal extract of the distillate was dried, evaporated, and the residue, which distilled almost completely below $85^\circ/20$ mm., three times fractionated over sodium.

The *d*- Δ^3 :⁸⁽⁹⁾-*p*-menthadiene thus obtained distilled constantly at $182\text{--}183^\circ/760$ mm., and had an even lower rotation than the preparation made by the first process. 0.8410, made up to 20 c.c. with ethyl acetate, gave, in a 2-dcm. tube, $\alpha + 7.6^\circ$, whence $[\alpha]_D + 90.4^\circ$.

The authors wish to state that much of the heavy expense of this investigation was met by a grant from the Research Fund of the Royal Society.

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LXIII.—*The Optical Properties of Compounds Containing an Asymmetric "Quaternary" Carbon Atom. Part I. The Synthesis of β -Phenyl- β -methylvaleric Acid and of as-Methylethylsuccinic Acid.*

By JOHN KENNETH HAROLD INGLIS.

ALTHOUGH it has been known for many years that an optically active compound often loses its activity on keeping, or on treatment with certain reagents, yet very little has been discovered in regard to the mechanism by which such changes take place. Now, in most optically active compounds hitherto investigated, one of the four groups of the asymmetric grouping is a hydrogen atom or a halogen atom, or a hydroxyl group. If the asymmetric group-

ing contained only groups which were less reactive than these, we should expect it to be correspondingly more stable as regards racemisation; and it therefore seemed that the study of the asymmetric "quaternary" carbon atom might throw some light on the mechanism underlying these changes. An increased stability for such a class of compound is shown in the case of the camphoric acids. Here, of the two asymmetric carbon atoms, one is tertiary and the other quaternary. When an active form of camphoric acid is heated, only one of these groupings undergoes racemisation, the quaternary grouping being unchanged. Thus *d*-camphoric acid, on heating, gives some *l*-isocamphoric acid, and, similarly, *l*-camphoric acid gives some *d*-isocamphoric acid. The complete racemisation of *d*- or *l*-camphoric acid does not appear to take place. The behaviour of such a substance therefore showed that the study of compounds which owed their whole activity to an asymmetric quaternary carbon atom might be profitable.

The first type of compound investigated was one in which the four groups of the asymmetric grouping were an acid group and three hydrocarbon radicles. An acid group was necessary to ensure the substance being easily resolved by means of alkaloids. It was necessary also to have a crystalline substance, in order that it might be easily purified. An acid containing a carbon atom linked to the four groups methyl, ethyl, phenyl, and $\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, was therefore prepared by the following series of reactions. Acetophenone was treated with magnesium ethyl bromide, and the tertiary alcohol isolated. This alcohol, on treatment with hydrogen chloride, gave the corresponding chloride, which, however, could not be purified by distillation, and was therefore used in the crude state. The crude chloride, on treatment with sodiomalonic ester, gave a small yield of a derivative of malonic ester, from which, after saponification, the corresponding acid could be obtained. This acid could be purified by recrystallisation, and, on heating, lost carbon dioxide and gave the required acid.

This acid, however, has shown itself unsuited for further experiment. It is a liquid at the ordinary temperature, and does not even form well-crystallising salts, except with quinine. The brucine salt, for example, could only be obtained as an oil. Fractional crystallisation, however, of the quinine salt did not appear to give a resolution of the acid. An equally unsatisfactory result was obtained with the closely-related acid containing a propyl group in place of the ethyl. A small quantity of this acid was prepared, but it also seemed to be a liquid. It was, therefore, not more closely studied.

As these monobasic acids had thus shown themselves unsuited

for the experiments in view, an investigation has been made of an acid of a somewhat different type. *as*-Methylethylsuccinic acid has already been prepared in several ways, and shown to be a crystalline solid melting at 104°. The most convenient method of preparation seemed to be that due to Higson and Thorpe (Trans., 1906, **89** 1467). According to these authors, if the sodium derivative of cyanoacetic ester suspended in alcohol is treated with the cyanohydrin of methyl ethyl ketone, an 80 per cent. yield is obtained of ethyl $\alpha\beta$ -dicyano- β -methyl- β -ethylpropionate (ethyl $\alpha\beta$ -dicyano- β -methylvalerate), an oil boiling at 162°/20 mm. This oil, on hydrolysis, gives a good yield of methylethylsuccinic acid. I have employed their method of preparation on several occasions, but have been unable to obtain a better yield than 40 per cent. The oil obtained boiled at 165°/19.5 mm., and on analysis proved to be pure. In Higson and Thorpe's experiments, the product, judging from the results of the analysis, must have been far from pure.

as-Methylethylsuccinic acid is readily soluble in water, and forms crystalline salts with brucine and quinine. The quinine salt, on fractional crystallisation, can be separated into two fractions, from which the active forms of the acid may be obtained. The brucine salt, on the other hand, is very easily soluble in water, and fractional crystallisation did not apparently effect a resolution.

Preparation of Phenylmethylethylcarbinol.

This alcohol was first obtained by Klages (*Ber.*, 1902, **35**, 3506) in the preparation of a styrene by the action of magnesium ethyl iodide on acetophenone. He did not, however, obtain the substance in a very pure state. The following process was found to give a satisfactory result: 24.4 grams of magnesium (1 atom) were dissolved in a mixture of about 110 grams of ethyl bromide (1 mol.) and 500 c.c. of dry ether. When all the magnesium had dissolved, the solution was cooled, and a solution of 115 grams of acetophenone (1 mol.) in 500 c.c. of dry ether was added slowly, the mixture being well shaken and the temperature kept below 10°. When all had been added, the mixture was left to remain in ice for 1½ hours. Excess of ice and hydrochloric acid were then added slowly. The ethereal solution was separated, washed well with aqueous sodium hydroxide, and then kept over solid potassium hydroxide. The dry ethereal solution was then distilled, and, after the ether had been removed, the distillation was continued under 20 mm. pressure, most of the liquid then passing over at 107—112°. It was found that if every trace of acid was not removed, the alcohol decomposed, even on distillation under diminished pressure, into olefine and

water. A small amount of decomposition took place, even when there was no acid present; but distillation under a lower pressure gave, finally, a nearly pure specimen, boiling at $106.5\text{--}108.5^\circ/15\text{ mm.}$ (Found, $C=79.8$; $H=9.37$. Calc., $C=80.0$; $H=9.3$ per cent.)

Preparation of Phenylmethylethylcarbinyl Chloride.

This substance was also prepared by Klages (*loc cit.*) by the action of hydrogen chloride on the alcohol. It was found to decompose on distillation, even in a vacuum. The crude chloride, therefore, diluted with ether, was washed free from acid, and, after drying, the ether was removed by distillation in a vacuum up to 40° . The bromide was also prepared, but was no more stable. The percentage of halogen was estimated by boiling with dilute nitric acid and an excess of standard silver nitrate, the excess of silver being determined by means of thiocyanate. The purest specimen of the chloride contained $Cl=19.6$, whereas $C_{10}H_{13}Cl$ requires $Cl=21.1$ per cent. The purest specimen of the bromide contained $Br=34.6$; Calc., $Br=37.5$ per cent.

Condensation of the Chloride with Sodiomalonic Ester.

This reaction was carried out under various conditions, but in no case was a good yield of condensation product obtained. Most of the chloride was converted into the olefine, and only a small portion condensed with the malonic ester. The following procedure gave the best yield: 4.6 grams of sodium were dissolved in 50 c.c. of alcohol, and 36 grams (a slight excess) of malonic ester added. This mixture was cooled to the ordinary temperature, and an amount of crude chloride, containing 33 grams of pure chloride, was added. The mixture was left for twenty hours, and then heated on the water-bath for four hours. The alcohol was then distilled off, water added, the oil was extracted with ether, and the ethereal solution dried. After removal of the ether, the distillation was continued under diminished pressure, most of the liquid boiling at $95\text{--}105^\circ/25\text{--}30\text{ mm.}$; but a small fraction remained in the flask, and finally boiled at $190\text{--}200^\circ/25\text{ mm.}$ The weight of this fraction was 4–5 grams. Several portions of this substance obtained in this way were mixed and redistilled, when the boiling point was $182\text{--}187^\circ/16\text{ mm.}$ This oil was not analysed, but was immediately saponified by heating with 40 per cent. potassium hydroxide and a little alcohol on the water-bath. In about one hour the saponification was complete, and from the liquid after dilution with water and acidifying with hydrochloric

acid, an acid was extracted which dissolved easily in warm water, but separated as an oil on cooling. This oil became crystalline after some time, and after repeated crystallisation melted at $134.5-136^{\circ}$:

0.1762 gave 0.4288 CO_2 and 0.1124 H_2O . $\text{C}=66.36$; $\text{H}=7.10$.

0.0892 (silver salt) gave 0.0428 Ag. Equiv. of acid = 118.

$\text{C}_{13}\text{H}_{16}\text{O}_4$ requires $\text{C}=66.1$; $\text{H}=6.78$ per cent. Equiv. = 118.

It is evident, therefore, that the condensation product was the ester of α -phenyl-sec.-butylmalonic acid,



In the above condensation the bulk of the substance was recovered as a liquid boiling at $95-105^{\circ}/25-30$ mm. This consisted of a mixture of malonic ester and the olefine, $\text{CH}_3 \cdot \text{CH} \cdot \text{CMePh}$, prepared by Klages (*loc. cit.*). This olefine, on treatment with hydrobromic acid, yielded an oil, which, on condensing with sodiomalonic ester and subsequent treatment as before, gave further quantities of apparently the same acid; for the two substances melted at almost exactly the same temperature as a mixture of them. Hence we may conclude that the olefine combines with hydrogen bromide to give the same bromide as would be obtained from the alcohol.

Preparation of β -Phenyl- β -methylvaleric Acid.

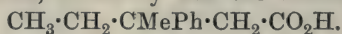
The malonic acid derivative, on being heated, began to lose carbon dioxide at a temperature slightly above its melting point. There remained an oil which showed at the ordinary temperature no signs of crystallisation. On cooling a solution in dry ether, crystals were formed, but could not be isolated. They appeared to melt below 0° . The acid was distilled under diminished pressure, and boiled at $174^{\circ}/14$ mm. The sodium salt was prepared, but did not crystallise from water. It was readily soluble in alcohol, but could not be recovered from it in a pure crystalline form. The silver salt was therefore prepared and analysed:

0.2173 gave 0.0780 Ag. $\text{Ag}=35.9$.

0.2257 „ 0.3983 CO_2 , 0.1042 H_2O , and 0.0812 Ag. $\text{C}=48.1$;
 $\text{H}=5.1$; $\text{Ag}=36.0$.

$\text{C}_{12}\text{H}_{15}\text{O}_2\text{Ag}$ requires $\text{C}=48.2$; $\text{H}=5.0$; $\text{Ag}=36.1$ per cent.

The acid, therefore, evidently has the formula



Attempted Resolution of the Acid.

When the acid was dissolved in sodium hydroxide, the excess of alkali neutralised with hydrochloric acid, and a solution of

quinine hydrochloride added, a gummy precipitate was formed, which rapidly became solid. This was collected, and found to be sparingly soluble in boiling water, and to crystallise out on cooling. It was, however, very readily soluble in absolute alcohol, and was recrystallised by adding small quantities of water to a concentrated alcoholic solution. The salt melted at $86-88^{\circ}$, and was repeatedly crystallised from aqueous alcohol in order to effect a resolution. The various fractions, however, had approximately the same melting point and specific rotation, showing that no resolution had taken place.

Synthesis of α -Phenyl- α -methylbutylmalonic Acid.

Phenylmethylpropylcarbinol was prepared by Klages (*Ber.*, 1902, **35**, 2643) by the action of magnesium propyl iodide on acetophenone. Under the action of hydrogen chloride it gives the chloride, which, like the other chlorides of this type, decomposes on distillation. Fifteen grams of this chloride were prepared and condensed with sodiomalonic ester. The mixture was left overnight, and then heated for six hours on the water-bath. The alcohol having been distilled off, water was added. The oil which separated was extracted with ether, and washed and dried as usual. After removal of the ether, the residual oil was distilled under 12 mm. pressure, and most of it passed over below 110° , only a small fraction remaining when the temperature reached 150° . This residual oil was then hydrolysed with 40 per cent. aqueous potassium hydroxide, and thus yielded about 0.7 gram of an acid, which could be crystallised from water, and then melted at $124-126^{\circ}$:

0.1910 gave 0.4654 CO_2 and 0.1311 H_2O . $\text{H} = 7.6$; $\text{C} = 66.4$.

$\text{C}_{14}\text{H}_{18}\text{O}_4$ requires $\text{C} = 67.2$; $\text{H} = 7.2$ per cent.

The acid was evidently not pure, but from its synthesis and analysis had the constitution $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMePh} \cdot \text{CH}(\text{CO}_2\text{H})_2$. As on heating it to expel carbon dioxide a liquid acid resulted, a closer examination of it was not made.

Condensation of Methyl Ethyl Ketonecyanohydrin and Sodiocyanoacetic Ester.

The cyanohydrin was prepared according to the method given by Ultee (*Rec. trav. chim.*, 1909, **28**, 1), and 25 grams of it were condensed with the sodium derivative of cyanoacetic ester according to Higson and Thorpe's directions (*loc. cit.*). After twelve hours, water was added, the liquid acidified, and extracted with ether. The ethereal solution was washed with dilute sodium carbonate and again with water, and then dried over calcium chloride. The ether having been distilled off, the residue was dis-

tilled under diminished pressure, a lower fraction, consisting mainly of cyanoacetic ester, and a higher fraction, boiling at $140\text{--}170^{\circ}/20$ mm., being thus obtained. This fraction of high boiling point consisted mainly of impure ethyl $\alpha\beta$ -dicyano- β -methylvalerate, and weighed 17—18 grams, the yield thus being about 36 per cent. This yield was hardly improved by using the method employed by Higson and Thorpe in the case of acetonecyanohydrin, namely, using excess of ethyl cyanoacetate, and adding the sodium derivative to an alcoholic solution of the cyanohydrin. Similarly, there was no improvement in the yield when the reaction was carried out below 0° .

The liquid boiling at $140\text{--}170^{\circ}/20$ mm. was redistilled, and then boiled at $164\text{--}166^{\circ}/19\cdot5$ mm.:

0.2287 gave 0.5158 CO_2 and 0.1498 H_2O . $\text{C}=61\cdot5$; $\text{H}=7\cdot26$.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C}=61\cdot8$; $\text{H}=7\cdot2$ per cent.

The hydrolysis of this compound to *as*-methylethylsuccinic acid was effected by the method described by Higson and Thorpe, and was almost quantitative. The acid, after crystallisation from water, melted sharply at 104° .

The Resolution of as-Methylethylsuccinic Acid.

Experiments have been made with both the quinine and brucine salts of the acid, but only the former seems to make a resolution possible. In the case of the brucine salt which is very soluble in water, two fractions were obtained of different melting point; but they had approximately the same specific rotation, and each fraction yielded the inactive acid. The quinine salt can be crystallised from water, in which it is only moderately soluble, and the less soluble fractions gave an acid which was dextrorotatory. As, however, only small quantities of the active acid have been obtained, and it was not free from the racemic form of the acid, no details as regards specific rotation can be given.

Further experiments are being made on the resolution of the acid, and when the active forms have been obtained in the pure state, the racemisation phenomena will be studied.

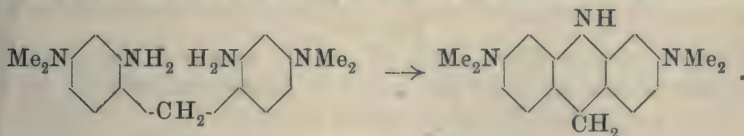
UNIVERSITY COLLEGE,
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LXIV.—*Fluorone Derivatives.*

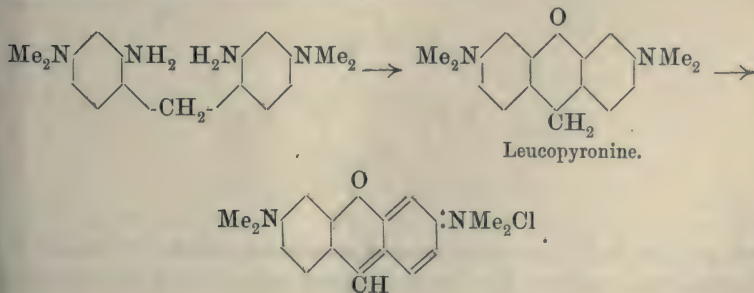
By FRANK GEORGE POPE and HUBERT HOWARD.

IN our last communication (Trans., 1910, **97**, 1023) we described certain derivatives of phenylfluorone, and gave reasons for preferring the para-quinonoid structure of such substances, rather than the ortho-quinonoid form advocated by Kehrman. We have now obtained other derivatives of phenylfluorone and phenylfluorime, and are able to give, as it seems to us, other arguments against the ortho-quinonoid formulation of such compounds.

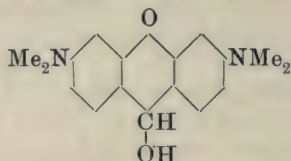
The first fluorime to be prepared was Pyronine-G, or tetramethylaminofluorime, which was obtained by Bender (D.R.-P. 59003), whilst its constitution was settled by Biehringer (*J. pr. Chem.*, 1896, [ii], **54**, 232), who prepared it by the oxidation of the product formed on condensation of formaldehyde and dimethyl-*m*-aminophenol. The constitution of this compound was deduced in the following manner. The tetramethyldiaminodiphenylmethane formed by the condensation of formaldehyde and dimethyl-*m*-aminophenol was nitrated, and the nitro-groups were then reduced to amino-groups. The resulting amino-compound, by elimination of ammonia, was converted into a dihydroacridine, which must consequently be represented as being produced in the following manner:



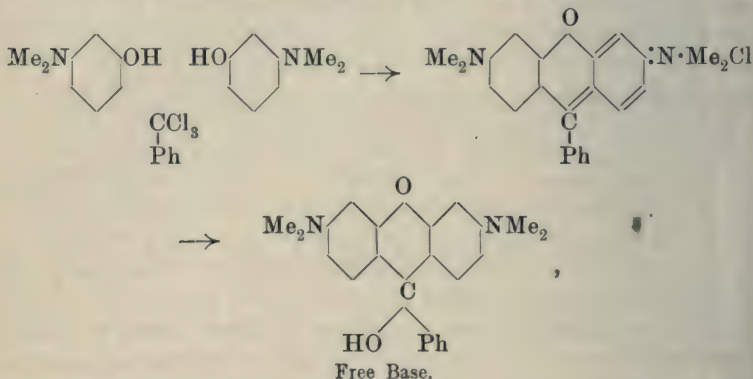
When the tetramethyltetra-aminodiphenylmethane was diazotised and the solution boiled, leucopyronine was produced, and this oxidised readily in acid solution to form pyronine salts. From this method of formation it was considered that the substances obtained possessed a para-quinonoid configuration:



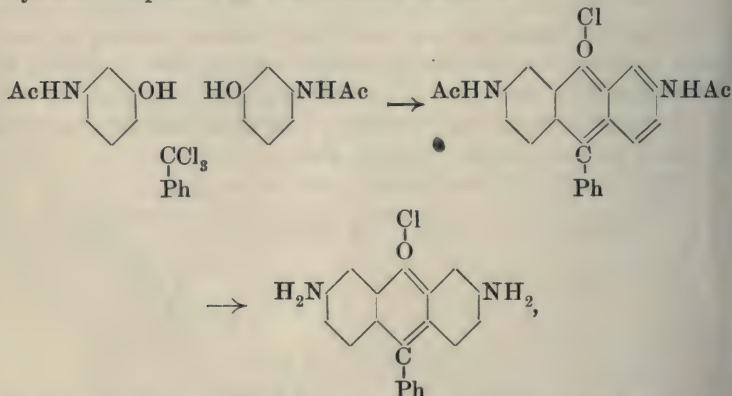
Similar substances have been obtained by Möhlau and Koch (*Ber.*, 1894, **27**, 2895), and it has been shown that on treatment with alkali hydroxide they yield ψ -bases of the type:



The rosamine bases are derivatives of phenylfluorime, a tetramethylrosamine (3:6-tetramethyldiamino-9-phenylxanthenyl chloride) being obtained by Heumann from the action of benzotrichloride on dimethyl-*m*-aminophenol in benzene solution:

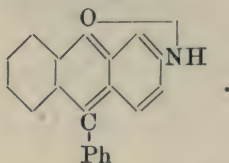


whilst Kehrman (*Ber.*, 1908, **41**, 3440) prepared the simplest member of the series by the action of benzotrichloride on monoacetyl-*m*-aminophenol in nitrobenzene solution:

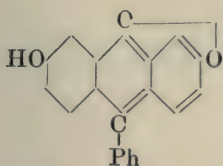


and gave to it the ortho-quinonoid structure, chiefly by reason of the analogy between rosamines and *aposafranone*. On diazotisation

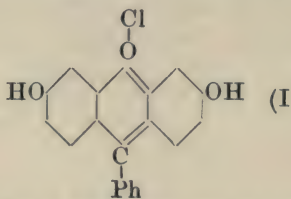
in acid solution he obtained from it hydroxyphenylfluorone, and he also showed that on treatment with alkali hydroxide it yielded an unstable ψ -base which rapidly lost water, and was converted into an anhydro-base, to which he assigned the following structure:



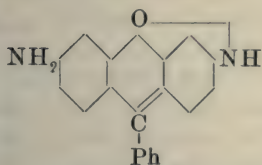
It certainly seems strange that he should here use the oxonium type in preference to the ammonium type of structure, since the basic properties of nitrogen are definite, whilst the existence of oxonium salts is not at present universally accepted. Again, if Kehrman's oxonium structure is correct, one would expect that rosamine chloride should be similar to hydroxyphenylfluorone hydrochloride and to the dichloroxanthonium chloride obtained by us:



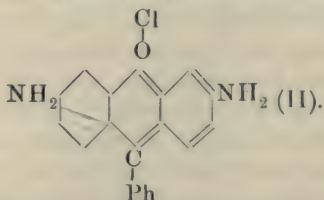
Hydroxyphenylfluorone (Kehrman).



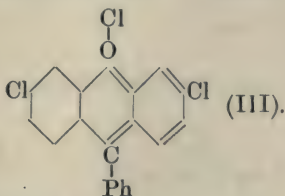
Hydroxyphenylfluorone hydrochloride.



Rosamine anhydro-base (Kehrman).



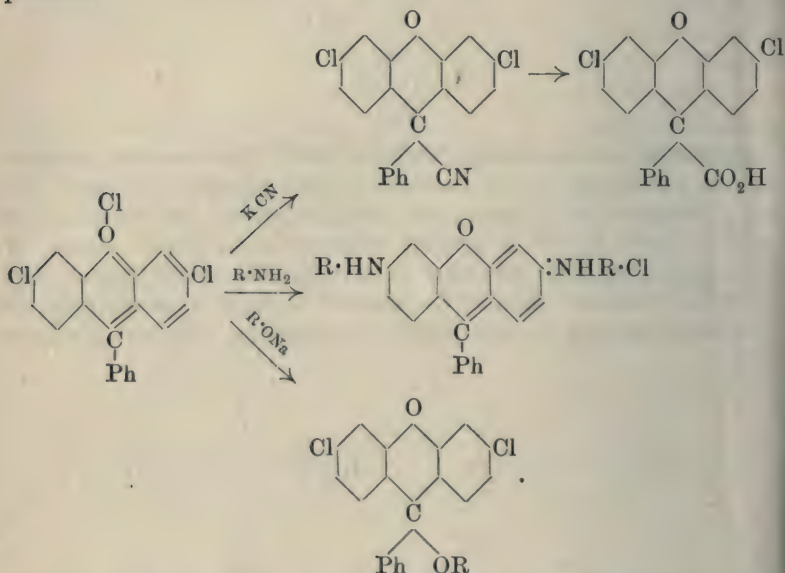
Rosamine chloride.



Dichlorophenylxanthonium chloride.

The three compounds (I, II, III) being all oxonium salts, should show similar behaviour, since the nucleus substituent groups can hardly exert any influence. In reality, we find that phenyl-

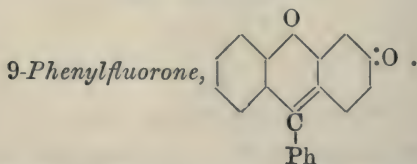
fluorone hydrochloride is readily hydrolysed in aqueous solution, rosamine chloride is the chloride of a strong base, and that dichloroxanthonium chloride is extremely reactive, as is shown by the following scheme of transformations which we have been able to perform:



Consequently it seems to us, taking these facts into consideration, that an ortho-quinonoid configuration for the fluorones is untenable.

It may be objected that our formation of compounds of the rosamine type from the xanthonium chloride is an argument in favour of the ortho-quinonoid formation, but it should be pointed out that a change of structure, with shifting of the "oxonium" chlorine atom, must occur, since in the formation of nitriles, acids, and ethers even the most staunch supporter of the oxonium structure would hardly attach cyano-, carboxy-, and alkyloxy-groups to the quadrivalent oxygen atom.

EXPERIMENTAL.



Two grams of anhydrous zinc chloride were heated with 2.16 grams of dihydroxybenzhydrol and 0.94 gram of phenol for

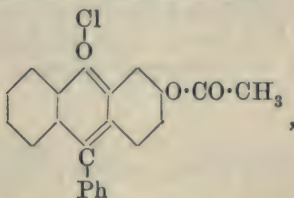
four hours to 160° . The fusion was extracted with hot water, dissolved in sodium hydroxide solution (in presence of zinc dust), the solution filtered, and the resulting hydroxyxanthen precipitated by dilute acetic acid. It was then collected, well washed with water, and redissolved in dilute sodium hydroxide solution. A stream of air was then drawn through the liquid for some days, when a precipitate of the fluorone was gradually produced. The precipitate was collected, washed, dried, and recrystallised from alcohol:

0.1118 gave 0.3428 CO_2 and 0.0452 H_2O . $\text{C}=83.63$; $\text{H}=4.49$.

$\text{C}_{19}\text{H}_{12}\text{O}_2$ requires $\text{C}=83.82$; $\text{H}=4.41$ per cent.

9-Phenylfluorone separates from alcohol in brown scales, which possess a green reflex. It is quite insoluble in aqueous alkali hydroxides, and even in dilute solutions of the mineral acids. It is soluble in concentrated sulphuric acid, the solution being dark brown in colour. From this solution it may be reprecipitated by the addition of water, as an orange powder. It melts at 200° , is soluble in hot alcohol, chloroform, or pyridine, but insoluble in light petroleum.

3-Acetoxy-9-phenylxanthonium chloride,



was obtained by dissolving 2.72 grams of phenylfluorone in chloroform and adding 0.78 gram of acetyl chloride to the liquid. The solution was poured into light petroleum, the yellow precipitate collected, washed with light petroleum, and dried in a vacuum:

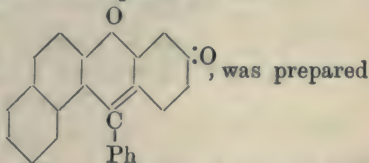
0.0916 gave 0.240 CO_2 and 0.0332 H_2O . $\text{C}=71.46$; $\text{H}=4.03$.

0.1060 „ 0.0440 AgCl . $\text{Cl}=10.27$.

$\text{C}_{21}\text{H}_{15}\text{O}_3\text{Cl}$ requires $\text{C}=71.89$; $\text{H}=4.28$; $\text{Cl}=10.13$ per cent.

The chloride is a yellow solid which decomposes at 130° .

11-Phenylphenonaphthafluorone,



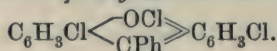
from the corresponding xanthen by drawing a stream of air through its alkaline solution. The precipitate was collected, well washed, and recrystallised from alcohol:

0.1100 gave 0.3450 CO_2 and 0.0436 H_2O . $\text{C}=85.54$; $\text{H}=4.40$.

$\text{C}_{23}\text{H}_{14}\text{O}_2$ requires $\text{C}=85.71$; $\text{H}=4.35$ per cent.

It separates from alcohol in brown scales, possessing a green reflex, and melts at 237° .

3:6-Dichloro-9-phenylxanthonium Chloride,



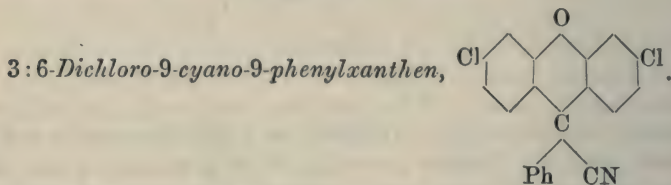
Five grams of hydroxyphenylfluorone were dissolved in 20 grams of phosphoryl chloride, and 10 grams of phosphorus pentachloride were then added. The blood-red liquid obtained was then heated on the water-bath until all the pentachloride had dissolved, allowed to remain for five minutes, and then poured, with constant stirring, into 300 c.c. of light petroleum. The reddish-coloured precipitate was collected, washed with light petroleum, and dried in a desiccator:

0.1068 gave 0.2464 CO_2 and 0.0276 H_2O . $\text{C}=62.92$; $\text{H}=2.87$.

0.1002 „ 0.1210 AgCl . $\text{Cl}=29.87$.

$\text{C}_{19}\text{H}_{11}\text{OCl}_3$ requires $\text{C}=63.07$; $\text{H}=3.04$; $\text{Cl}=29.49$ per cent.

The xanthonium chloride is a reddish-yellow solid which decomposes at about 200° . It is insoluble in non-hydroxylic solvents, and is rapidly decomposed by hydroxylic solvents.



In the preparation of this substance, 3 grams of dichlorophenylxanthonium chloride were heated on the water-bath with 0.6 gram of potassium cyanide and 20 c.c. of alcohol. The precipitated solid was collected, washed, and recrystallised from hot alcohol:

0.1170 gave 0.2940 CO_2 and 0.0332 H_2O . $\text{C}=68.53$; $\text{H}=3.15$.

0.1040 „ 0.0856 AgCl . $\text{Cl}=20.36$.

0.2654 „ 9 c.c. N_2 (dry) at 22° and 758 mm. $\text{N}=3.91$.

$\text{C}_{22}\text{H}_{11}\text{ONCl}_2$ requires $\text{C}=68.15$; $\text{H}=3.12$; $\text{Cl}=20.17$;

$\text{N}=3.98$ per cent.

The nitrile crystallises in minute, reddish-brown crystals, and is very sparingly soluble in hot alcohol or glacial acetic acid. It decomposes at 280° .

3:6-Dichloro-9-phenylxanthen-9-carboxylic acid was prepared by heating 10 grams of the nitrile with 150 c.c. of alcohol and 25 c.c. of

concentrated hydrochloric acid, under reflux, for two hours. On cooling, the acid separated as a microcrystalline powder. It was purified by dissolving in sodium carbonate, filtering the solution, and reprecipitating the acid with dilute hydrochloric acid, and, finally, recrystallisation from alcohol:

0.1142 gave 0.2690 CO_2 and 0.0374 H_2O . $\text{C}=64.24$; $\text{H}=3.64$.

0.1020 „ 0.0806 AgCl . $\text{Cl}=19.55$.

$\text{C}_{20}\text{H}_{12}\text{O}_3\text{Cl}_2$ requires $\text{C}=64.69$; $\text{H}=3.23$; $\text{Cl}=19.13$ per cent.

The free acid is a reddish-brown solid, which blackens when heated to about 300° . It is sparingly soluble in alcohol or acetic acid, and insoluble in hydrocarbon solvents. The *ethyl* ester was obtained by heating 1 gram of the acid with 5 grams of concentrated hydrochloric acid and 20 grams of alcohol under reflux for four hours. The solution was then poured out into sodium carbonate solution, and the precipitate collected, washed, and recrystallised from alcohol:

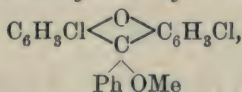
0.1076 gave 0.2616 CO_2 and 0.402 H_2O . $\text{C}=66.30$; $\text{H}=4.15$.

0.2340 „ 0.1680 AgCl . $\text{Cl}=17.76$.

$\text{C}_{22}\text{H}_{16}\text{O}_3\text{Cl}_2$ requires $\text{C}=66.17$; $\text{H}=4.01$; $\text{Cl}=17.80$ per cent.

The ester is a reddish-brown powder, which is sparingly soluble in alcohol or pyridine. It decomposes at about 200° .

3:6-Dichloro-9-phenylxanthyl methyl ether,



was prepared by adding 2 grams of the dichloroxanthonium chloride to the calculated quantity of sodium methoxide, dissolved in 25 c.c. of methyl alcohol. The solution was heated under reflux for half an hour, and then poured into 50 c.c. of water, the whole being boiled, and finally acidified with dilute acid. The precipitate was collected, washed, dried, and recrystallised from alcohol:

0.1226 gave 0.3042 CO_2 and 0.0420 H_2O . $\text{C}=67.67$; $\text{H}=3.50$.

0.1590 „ 0.1308 AgCl . $\text{Cl}=20.35$.

$\text{C}_{20}\text{H}_{14}\text{O}_2\text{Cl}_2$ requires $\text{C}=67.23$; $\text{H}=3.92$; $\text{Cl}=19.95$ per cent.

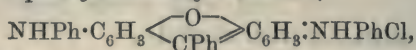
The ether decomposes at about 220° , and is a reddish-brown powder, which is sparingly soluble in the ordinary organic solvents.

The *ethyl* ether was prepared in a similar manner, and shows the same characteristics:

0.1105 gave 0.2740 CO_2 and 0.410 H_2O . $\text{C}=67.63$; $\text{H}=4.12$.

0.1130 „ 0.090 AgCl . $\text{Cl}=19.70$.

$\text{C}_{21}\text{H}_{16}\text{O}_2\text{Cl}_2$ requires $\text{C}=67.94$; $\text{H}=4.31$; $\text{Cl}=19.13$ per cent.

*Rosamine Derivatives.**3:6-Dianilino-9-phenylxanthenyl chloride,*

was obtained by heating 5 grams of dichlorophenylxanthonium chloride for five minutes with 25 c.c. of aniline. The resulting paste was then stirred into 200 c.c. of water, and the mixture rendered alkaline and distilled in steam to remove excess of aniline. The residual mixture was acidified, the precipitate collected, well washed, and recrystallised from alcohol:

0.1100 gave 0.3150 CO_2 and 0.0465 H_2O . $\text{C}=78.10$; $\text{H}=4.70$.

0.2040 „ 0.0600 AgCl . $\text{Cl}=7.28$.

0.3546 „ 16.4 c.c. N_2 (dry) at 23° and 765 mm. $\text{N}=5.38$.

$\text{C}_{31}\text{H}_{23}\text{ON}_2\text{Cl}$ requires $\text{C}=78.39$; $\text{H}=4.84$; $\text{Cl}=7.48$; $\text{N}=5.81$ per cent.

The rosamine chloride crystallises in small, bluish-purple needles, and is sparingly soluble in alcohol. Its solution possesses an intense green fluorescence.

3:6-Di-o-toluidino-9-phenylxanthenyl chloride is prepared in a similar manner from the dichloroxanthonium chloride and o-toluidine:

0.1002 gave 0.2982 CO_2 and 0.0488 H_2O . $\text{C}=81.17$; $\text{H}=5.40$.

0.2066 „ 0.584 AgCl . $\text{Cl}=6.99$.

0.350 „ 16 c.c. N_2 (dry) at 22° and 765 mm. $\text{N}=5.32$.

$\text{C}_{33}\text{H}_{27}\text{ON}_2\text{Cl}$ requires $\text{C}=81.39$; $\text{H}=5.55$; $\text{Cl}=7.06$; $\text{N}=5.58$ per cent.

It is a purple-red solid, which is somewhat soluble in alcohol, the solution showing an intense fluorescence.

3:6-Di-p-toluidino-9-phenylxanthenyl chloride was prepared in a similar manner from p-toluidine:

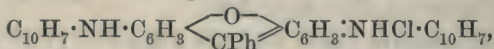
0.1102 gave 0.3276 CO_2 and 0.0535 H_2O . $\text{C}=81.08$; $\text{H}=5.39$.

0.200 „ 0.0564 AgCl . $\text{Cl}=6.98$.

0.3450 „ 16 c.c. N_2 (dry) at 22° and 765 mm. $\text{N}=5.40$.

$\text{C}_{33}\text{H}_{27}\text{ON}_2\text{Cl}$ requires $\text{C}=81.39$; $\text{H}=5.55$; $\text{Cl}=7.06$; $\text{N}=5.58$ per cent.

It resembles the ortho-compound in properties, but is somewhat darker in shade.

3:6-Di-β-naphthylamino-9-phenylxanthenyl chloride,

was obtained by heating dichlorophenylxanthonium chloride with an excess of β-naphthylamine. The product was poured into water,

rendered alkaline, and distilled in a current of steam. The residue was acidified, collected, washed, dried, and recrystallised from alcohol. It is a blue, microcrystalline solid, which is sparingly soluble in alcohol. It yields blue solutions, which show a violet fluorescence. When heated, it decomposes at 235° :

0.1008 gave 0.3018 CO_2 and 0.0444 H_2O . $\text{C}=81.65$; $\text{H}=4.89$.

0.1170 „ 0.0280 AgCl . $\text{Cl}=5.92$.

0.230 „ 10 c.c. N_2 (dry) at 22° and 761 mm. $\text{N}=5.04$.

$\text{C}_{39}\text{H}_{27}\text{ON}_2\text{Cl}$ requires $\text{C}=81.46$; $\text{H}=4.70$; $\text{Cl}=6.18$; $\text{N}=4.88$ per cent.

3:6-Di-*p*-aminophenylamino-9-phenylxanthenyl chloride was prepared in the form of its dihydrochloride by the condensation of *p*-phenylenediamine with dichlorophenylxanthonium chloride. The solution of the free base was evaporated to small bulk, and a large excess of concentrated hydrochloric acid added. The precipitated diamine hydrochloride was collected, the filtrate being concentrated and extracted with alcohol. The alcoholic solution was then evaporated, and the hydrochloride finally recrystallised from water:

0.090 gave 0.2246 CO_2 and 0.0398 H_2O . $\text{C}=68.06$; $\text{H}=4.91$.

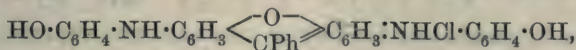
0.1230 „ 0.0934 AgCl . $\text{Cl}=18.78$.

0.1825 „ 15 c.c. N_2 (dry) at 22° and 760 mm. $\text{N}=9.76$.

$\text{C}_{31}\text{H}_{27}\text{ON}_4\text{Cl}_3$ requires $\text{C}=67.84$; $\text{H}=4.74$; $\text{Cl}=18.44$; $\text{N}=9.70$ per cent.

The hydrochloride crystallises in minute, blue needles, and is very soluble in water or alcohol.

3:6-Di-*p*-hydroxyphenylamino-9-phenylxanthenyl chloride,



is similarly obtained from dichloroxanthonium chloride and *p*-aminophenol. The fusion is dissolved in ammonia, the solution filtered, and acidified by hydrochloric acid. It is then evaporated to dryness, extracted by alcohol, filtered, and again evaporated. The residue is dissolved in sodium hydroxide solution, and again precipitated by carbon dioxide. The precipitate is then collected, dissolved in alcoholic hydrochloric acid, the solution again evaporated, and the residue finally crystallised from dilute alcohol. In this way it is obtained in small, dark reddish-purple needles, which dissolve in the alkali hydroxides with a deep violet colour:

0.1172 gave 0.3034 CO_2 and 0.0508 H_2O . $\text{C}=70.60$; $\text{H}=4.82$.

0.1040 lost 0.0035 H_2O at 130° . $\text{H}_2\text{O}=3.36$.

$\text{C}_{31}\text{H}_{23}\text{O}_3\text{N}_2\text{Cl}\cdot\text{H}_2\text{O}$ requires $\text{C}=70.92$; $\text{H}=4.77$; $\text{H}_2\text{O}=3.43$ per cent.

0.081* gave 4 c.c. N_2 (dry) at 17° and 752 mm. $N=5.77$.

0.1356* „ 0.0376 AgCl. $Cl=6.86$.

$C_{31}H_{23}O_3N_2Cl$ requires $N=5.56$; $Cl=7.01$ per cent.

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LXV.—*Synthesis of dl-3:4-Dihydroxyphenylalanine.*

By CASIMIR FUNK.

THE question of the formation of adrenaline in the animal body has engaged much attention. The two amino-acids that suggest themselves as the parent substances of adrenaline are obviously tyrosine and phenylalanine, but certain considerations render it probable that the body is incapable of employing these substances for the formation of adrenaline. Thus, in cases of abnormal metabolism, tyrosine is eliminated as homogentisic acid (Wolkow and Baumann, *Zeitsch. physiol. Chem.*, 1891, **15**, 228; Falta and Langstein, *ibid.*, 1903, **37**, 513; Abderhalden, Bloch, and Rona, *ibid.*, 1907, **52**, 435), whilst no catechol derivatives have been obtained from any of the aromatic amino-acids.

In the experiments which have been conducted on this point, investigators have sought to bring about a transformation of tyrosine (Ewins and Laidlaw, *J. Physiol.*, 1910, **40**, 275) into adrenaline by incubating the former substance with suprarenal gland tissue. It may well be, however, that the formation of adrenaline takes place in several steps, and that different tissues of the body are necessary.

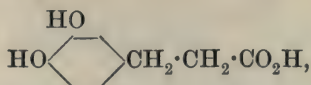
In order to be certain that adrenaline is really formed, it is necessary to find a chemical method by which this substance can be separated from amino-acids, and such a separation is at present being attempted.

That some substance of the nature of tyrosine or phenylalanine is the precursor of adrenaline is further suggested by the fact that all three compounds belong to the same optical (*l*) series.

The synthesis of 3:4-dihydroxyphenylalanine has been effected with the idea that it may be the parent substance of adrenaline; experiments are also being conducted in order to ascertain whether any of this substance is contained in proteins. That this may be

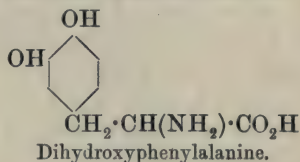
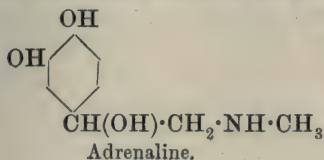
* Anhydrous substance.

the case is indicated by the occurrence of caffeic acids in plants. A dihydroxycaffeic acid,



has been found by Lippmann in turnip leaves (*Ber.*, 1892, **25**, 3220).

A comparison of the formulæ of adrenaline and dihydroxyphenylalanine indicates a certain similarity between these substances:

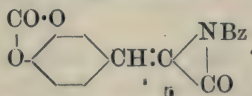


EXPERIMENTAL.

Synthesis of 3:4-Dihydroxyphenylalanine.

Dihydroxyphenylalanine was obtained according to the method described by Erlenmeyer and Halsey (*Annalen*, 1899, **307**, 138; *Ber.*, 1897, **30**, 2981) for the synthesis of tyrosine.

Condensation of 3:4-Carbonyldioxybenzaldehyde and Hippuric Acid: Lactimide of α -Benzoylamino-3:4-dihydroxycinnamic Acid,

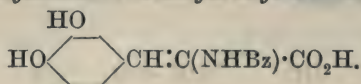


Sixty grams of 3:4-carbonyldioxybenzaldehyde were mixed with 66.5 grams of hippuric acid and 30 grams of anhydrous sodium acetate, and the mixture was heated for one hour on the water-bath with 112 grams of acetic anhydride. The solution became yellow, and in a short time a yellow, crystalline substance separated out. Owing to the insolubility of this substance in the ordinary solvents, it was found necessary to purify it by boiling, first with water and then with alcohol. The crystals obtained in this way consisted of small, yellow plates, which melted about 238°. Yield=83 grams, or 74 per cent. of the theoretical. After drying in a vacuum at 70°, the substance was analysed:

0.3116 gave 0.7604 CO₂ and 0.0906 H₂O. C=66.55; H=3.23.

0.4266, by Kjeldahl's method, required 13.5 c.c. N/10-H₂SO₄. N=4.43.

C₁₇H₉O₅N requires C=66.43; H=2.95; N=4.56 per cent.

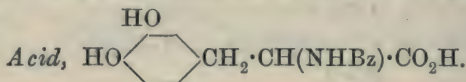
α -Benzoylamino-3:4-dihydroxycinnamic Acid,

Eighty-three grams of the lactimide prepared as above were heated on the water-bath with 500 c.c. of 10 per cent. sodium hydroxide solution. In this way, both the lactimide and carbonyldioxy-groups were hydrolysed. After cooling and neutralising with hydrochloric acid, a resinous mass separated out, which became crystalline after keeping for some time in the cold. This was twice recrystallised from alcohol, when small, yellow plates were obtained, which, on drying in a vacuum, melted at 210—215°. At 100° it sublimed to form colourless plates. The yield was 60 grams, or 75 per cent. of the theoretical:

0.2268 gave 0.5368 CO₂ and 0.0902 H₂O. C=64.55; H=4.31.

0.39, by Kjeldahl's method, required 12.2 c.c. N/10-H₂SO₄. N=4.35.

C₁₀H₁₃O₅N requires C=64.18; H=4.38; N=4.68 per cent.

Preparation of dl- α -Benzoylamino-3:4-dihydroxy- β -phenylpropionic

The 60 grams of the substance just described were suspended in 600 c.c. of water, and 750 grams of sodium amalgam added in small portions during forty-five minutes. The solution was neutralised with hydrochloric acid, and concentrated under diminished pressure in a stream of coal gas. Small, yellow, four-sided plates separated out. Yield, 19.6 grams, or 32 per cent. of the theoretical. By following the directions of E. Fischer (*Ber.*, 1899, **32**, 3638), who, in his work on tyrosine, boiled the corresponding solution with 33 per cent. aqueous sodium hydroxide, all this substance seemed to be destroyed.

The crystals were recrystallised from water, and contained one molecule of water of crystallisation, which was expelled when heated in a vacuum at 110°. They are sparingly soluble in cold, and readily so in hot, water, also in alcohol, glacial acetic acid, or ethyl acetate, but not in benzene. The anhydrous substance melts at 190—195°:

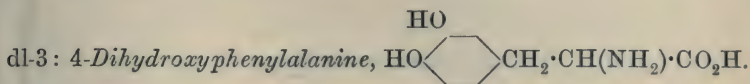
1.092 lost 0.0596 H₂O. H₂O=5.45.

C₁₆H₁₅O₅N, H₂O requires H₂O=5.64 per cent.

0.2616 gave 0.614 CO₂ and 0.1132 H₂O. C=64.01; H=4.80.

0.3248, by Kjeldahl's method, required 10.0 c.c. $N/10\text{-H}_2\text{SO}_4$.
 $N=4.30$.

$\text{C}_{16}\text{H}_{15}\text{O}_5\text{N}$ requires $C=63.75$; $H=5.03$; $N=4.65$ per cent.



18.2 Grams of the benzoyl compound were hydrolysed by boiling with sixty times its weight of 20 per cent. hydrochloric acid under a reflux condenser. The solution was left overnight in the cold, and the benzoic acid which separated out was collected. The filtrate was extracted with ether, and the aqueous solution concentrated in a vacuum. The residue obtained was dissolved in a small quantity of water, neutralised with ammonia, and concentrated under diminished pressure in an atmosphere of coal gas. On recrystallising from water, 5.7 grams of spindle-shaped crystals were obtained, corresponding with a yield of 47 per cent. of the theoretical. After being dried in a vacuum, the crystals melted at $263-272^\circ$:

0.21 gave 0.4218 CO_2 and 0.1042 H_2O . $C=54.75$; $H=5.51$.

0.1838, by Kjeldahl's method, required 9.0 $N/10\text{-H}_2\text{SO}_4$.
 $N=6.85$.

$\text{C}_9\text{H}_{11}\text{O}_4\text{N}$ requires $C=54.79$; $H=5.63$; $N=7.10$ per cent.

This substance is readily oxidised in neutral, and more readily in alkaline, solution, with the formation of a black pigment. With nitric acid, a red coloration is obtained. Millon's reagent in the cold gives an orange colour, but on heating, reduction takes place. With ferric chloride, a green colour is formed, which, on boiling or on the addition of ammonia, becomes dark red. The substance reduces Fehling's solution on heating. It dissolves in water more easily than does tyrosine, and gives a crystalline hydrochloride, but an ethyl ester hydrochloride could not be obtained.

I am at present preparing the active *l*-compound and some derivatives of it, and intend shortly to publish some experiments on the physiological action of these compounds. I wish to express my thanks to Dr. Harden for granting me the use of his laboratory.

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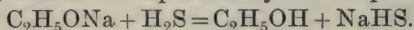
LXVI.—*The Action of Hydrogen Sulphide on the Alkyl-oxides of the Metals. Part I. Sodium and Potassium Ethoxides.*

By ALEXANDER RULE.

THE work described in this paper forms the first portion of an investigation of certain metallic salts, which, owing to hydrolysis, cannot be obtained from aqueous solution, and up to the present have only been prepared in the dry way. The sulphides of chromium, aluminium, and ferric iron are examples of such compounds, and it is doubtful if these substances have ever been obtained in the pure state.

The possibility of preparing these sulphides from alcoholic solution by precipitation with either hydrogen sulphide or an alcoholic solution of sodium sulphide suggested itself to the author, but it was necessary, in the first place, to find derivatives of the metals which were soluble in alcohol, and which, on decomposition according to the method indicated, would not give rise to products likely to react in any way on the sulphides, if the latter were formed.

The alkyloxides of the metals in question appeared to be suitable for trial in this way, but on endeavouring to ascertain if previous work had been done in this direction, the author was unable to find any record of the action of hydrogen sulphide, either on these compounds or on the alkyloxides of sodium or potassium. The action of certain other gases, such as carbon monoxide, on the alkyloxides of sodium and potassium is well known, and has been thoroughly investigated. When sodium is dissolved in absolute alcohol in such amount as to give a solution of sodium ethoxide of moderate concentration, and this solution is then saturated with dry hydrogen sulphide, no precipitate is formed, but on adding sufficient benzene or ether to the solution, a precipitate of practically pure anhydrous sodium hydrosulphide is obtained. A solution of potassium ethoxide, similarly treated, gives a precipitate of pure anhydrous potassium hydrosulphide. There is no indication of the formation of organic sulphur compounds, and from the results obtained under varied conditions, the reaction appears to be quantitative, and to be expressed by the simple equation:



In view of the considerable amount of work already done on the sulphides and hydrosulphides of the alkali metals, and the difficulty experienced in obtaining the anhydrous compounds in the pure

state, the investigation of this apparently simple method of preparation seemed of importance.

Gay Lussac and Thénard made an attempt to obtain the anhydrous hydrosulphides of sodium and potassium by the action of hydrogen sulphide on the heated metals. A brown mass was obtained, and to the sodium compound they ascribed the composition Na_3HS_2 . According to Sabatier, these products always contain polysulphides.

Sabatier (*Ann. Chim. Phys.*, 1881, [v], **22**, 1) states that anhydrous sodium hydrosulphide is obtained by saturating crystals of sodium sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, with hydrogen sulphide, and evaporating the solution obtained in a current of hydrogen sulphide. The product is described as a yellowish-white mass, nearly pure. Bloxam (*Trans.*, 1900, **77**, 763) found, however, that sodium sulphide was only slowly acted on by hydrogen sulphide in the solid state, and failed to obtain sodium hydrosulphide by this method.

From the foregoing evidence it seems practically certain that the pure hydrosulphides are unobtainable by any of the methods mentioned. Bloxam (*loc. cit.*) describes a method suggested by Dr. Scott for the preparation of anhydrous potassium hydrosulphide. Hydrogen sulphide was passed into rectified ether containing metallic potassium, and in this way the hydrosulphide was obtained pure as a pale yellow, crystalline powder.

The use of alcohol as a solvent for sodium hydroxide in the ordinary method for the preparation of sodium monosulphide is described by Böttger (*Annalen*, 1884, **223**, 335), but the resulting product was hydrated, owing to the formation of water by the action of hydrogen sulphide on the sodium hydroxide in solution.

The author of the present paper has also investigated the action of hydrogen sulphide on the pure dry ethoxides of sodium and potassium. In each case reaction takes place in the cold, the sole products being alcohol and the hydrosulphides of the metals. There is no evidence of the formation of the monosulphides, as is the case when hydrogen sulphide is allowed to act on dry sodium hydroxide (Kircher, *Annalen*, 1839, **31**, 339).

The simple reaction whereby anhydrous sodium hydrosulphide is obtained in alcoholic solution will doubtless prove of considerable value in the preparation of organic sulphur compounds, where, ordinarily, crystalline sodium hydrosulphide is employed. In these cases the presence of water of hydration, and often of free sodium hydroxide in the salt, occasions loss through hydrolysis.

EXPERIMENTAL.

For analysis of the hydrosulphides dealt with in this section, gravimetric methods were employed in every case. Owing to the extremely hygroscopic character of these substances, it was found necessary to carry out weighing operations with special care and rapidity. Sulphur was estimated by oxidation with concentrated bromine water, and precipitation as barium sulphate. Sodium and potassium were estimated as sulphates, but before the addition of sulphuric acid to the substances they were treated with bromine water. Otherwise, the violent evolution of hydrogen sulphide on adding acid is liable to cause loss.

The action of hydrogen sulphide on sodium ethoxide in alcoholic solution can be illustrated very rapidly on a small scale by dissolving 0.5 gram of metallic sodium in about 10 c.c. of ethyl alcohol in a test-tube, adding an equal volume of dry benzene, and then passing in the gas. The solution becomes warm, and after a short time a precipitate begins to separate out, becoming thicker as the passage of the gas is continued. When the solution is saturated with the gas, the product is rapidly collected, washed with a little ether, and then placed immediately in a dessicator and allowed to remain in a vacuum. The substance obtained by this method possesses a light buff tint, is extremely deliquescent, and when freshly prepared dissolves in hydrochloric acid to a clear solution with violent evolution of hydrogen sulphide.

A similar experiment with potassium ethoxide gives a product quite analogous to the sodium compound, but only very faintly buff-coloured.

If the solution, after collecting the precipitate, is treated with a further quantity of benzene, or, better, with dry ether, a considerable precipitate is obtained, which is identical in properties and composition to the first product. It was obvious that in order to obtain a maximum yield, careful regulation of the relative amounts of alcohol and precipitant would be necessary.

Action of Hydrogen Sulphide on a Saturated Solution of Sodium Ethoxide.

Two grams of sodium were added to 20 c.c. of absolute ethyl alcohol (freshly distilled over lime) in a small flask fitted to a reflux condenser. When sodium ethoxide began to separate out, more alcohol was added, until just sufficient was present to retain the product in solution at room temperature. Forty c.c. of alcohol were required. The flask was then furnished with a tightly-fitting

cork, through which passed a delivery tube and an exit tube with calcium chloride bulb attached. Hydrogen sulphide, washed by passing through water, and then dried over a long column of calcium chloride, was passed into the solution in a rapid stream, and after a few minutes a fine crystalline precipitate began to form in the solution, and increased with continued passage of the gas.

When the solution was saturated with hydrogen sulphide, the precipitate was collected as rapidly as possible, sprayed with absolute alcohol, and kept in a vacuum over calcium chloride. The substance thus obtained was buff-coloured. It weighed 0.25 gram. For analysis a larger quantity was prepared under precisely similar conditions:

0.2514 gave 0.3142 Na_2SO_4 . $\text{Na}=40.48$.

0.2641 „ 1.0721 BaSO_4 . $\text{S}=55.84$.

NaHS requires $\text{Na}=41.07$; $\text{S}=57.14$ per cent.

The product is slightly impure sodium hydrosulphide, and there is no indication that double compounds of sodium ethoxide and monosulphide are formed in the course of the reaction, as the precipitate does not dissolve on continued passage of the gas, but increases in amount (compare Bloxam, *loc. cit.* Preparation of sodium monosulphide). This substance was found to contain a trace of iron, which appears to be an impurity of metallic sodium, and probably causes the coloration of the substance.

The filtrate from the above product was quickly transferred to a dry flask, and 50 c.c. of pure dry ether were added. A pure white, crystalline precipitate was immediately formed. The flask was corked and kept in a desiccator until the precipitate had settled, and a further quantity of ether was added, this operation being repeated until the addition of ether produced only a slight turbidity in the supernatant liquid: 110 c.c. of ether were used. The product was collected, washed with dry ether, and kept in a vacuum for several hours. Further addition of ether to the filtrate only produced a faint cloud.

The substance was a pure white, granular powder:

0.1598 gave 0.2010 Na_2SO_4 . $\text{Na}=40.74$.

0.1795 „ 0.7398 BaSO_4 . $\text{S}=56.71$.

NaHS requires $\text{Na}=41.07$; $\text{S}=57.14$ per cent.

4.31 Grams were obtained; thus the total yield of sodium hydrosulphide from 2 grams of sodium $=4.31+0.25=4.56$. Theory requires 4.86 grams. (A slight loss occurred through a little of the substance sticking to the sides of the flask; owing to its hygroscopic nature it was neglected.) The reaction, therefore, appears

to be quantitative, but the amount of ether required to precipitate the product completely is considerable. The ether is, however, very easily recoverable in the pure state.

The freshly prepared compound dissolved to a clear solution in hydrochloric acid, with vigorous evolution of hydrogen sulphide. After the substance had been kept for a few days, a solution so obtained was faintly opalescent, owing to separation of a trace of sulphur derived from products of slight oxidation. The substance is extremely soluble in water, and moderately so in alcohol. On allowing it to remain in the air for a few moments, a faint odour of hydrogen sulphide is noticeable. It deliquesces very rapidly, forming an almost colourless solution, from which colourless crystals separate out after a few days (compare Bloxam, *loc. cit.*).

Action of Hydrogen Sulphide on Sodium Ethoxide Suspended in Benzene.

For the preparation of larger quantities of sodium hydrosulphide, it was found more convenient to carry out the reaction in presence of the precipitant. Ether is unsuitable for this purpose on account of its volatility, but good results were obtained with benzene.

One hundred c.c. of pure dry benzene were mixed with 10 grams of absolute alcohol in a flask fitted with a reflux condenser, the inner tube of which was ground to fit the mouth of the flask. Five grams of metallic sodium in small pieces were introduced into the mixture, which was then heated to boiling on the water-bath. As the reaction slowed, further quantities of alcohol were added, until the sodium was completely dissolved. On allowing to cool, sodium ethoxide separated out as a gelatinous mass. Dry hydrogen sulphide was passed in, and reaction took place immediately with considerable evolution of heat and the formation of a fine crystalline precipitate of sodium hydrosulphide. The passage of the gas was continued until the precipitate had settled, and no further turbidity was produced in the supernatant liquid. The product was collected, washed with dry benzene, and finally with dry ether, which caused a slight precipitation in the filtrate. After remaining for one day in a vacuum, it weighed 11.92 grams. Theory requires 12.15 grams. Yield = 98.1 per cent.:

0.2720 gave 0.3386 Na_2SO_4 . $\text{Na} = 40.32$.

0.2429 „ 0.9992 BaSO_4 . $\text{S} = 56.49$.

NaHS requires $\text{Na} = 41.07$; $\text{S} = 57.14$ per cent.

The substance was slightly buff-coloured, but in all other respects identical with that obtained by precipitation with ether. It was found somewhat difficult to remove the last traces of benzene from

the product, which still possessed a faint odour of the hydrocarbon after remaining in a vacuum for a week. It was finally expelled by heating the substance to 110° in a slow current of hydrogen.

Action of Hydrogen Sulphide on Solid Sodium Ethoxide.

One gram of metallic sodium was dissolved in absolute alcohol contained in a small distillation flask of known weight fitted to a condenser. Excess of alcohol was distilled off, and the product then heated gradually to 180° in an oil-bath, in a current of dry hydrogen, until no more alcohol passed over. Sodium ethoxide was obtained in this way as a perfectly homogeneous, white mass. The contents of the flask were then allowed to cool in hydrogen, and when quite cold, dry hydrogen sulphide was passed into the flask. The ethoxide immediately began to assume a light buff tint, which quickly spread over its surface. The mass became hot, alcohol was evolved, and condensed on the walls of the flask. After passage of the gas had continued for about twenty minutes, it was possible to detach a considerable portion of the substance from the glass by tapping the flask. The product was very light pink, and appeared homogeneous, except where it had been in contact with the glass; these portions were dirty white on the surface.

The substance was heated gradually to 90° in a current of hydrogen. Alcohol commenced to distil over, and continued up to 120° . At this temperature the escaping gas was tested, and found to contain traces of hydrogen sulphide, and in order to prevent possible decomposition of sodium hydrosulphide at higher temperatures, the heating was continued in a slow stream of hydrogen sulphide to 180° , during which the last traces of alcohol were driven over. The flask was then allowed to cool, tightly stoppered, and weighed. Weight of product = 2.41 grams. Theory requires 2.43 grams for 1 gram of sodium:

0.2866 gave 0.3751 Na_2SO_4 . $\text{Na} = 42.43$.

0.1656 „ 0.2170 Na_2SO_4 . $\text{Na} = 42.44$.

0.3506 „ 1.4205 BaSO_4 . $\text{S} = 55.64$.

NaHS requires $\text{Na} = 41.07$; $\text{S} = 57.14$ per cent.

The substance dissolved in water, giving a faintly yellow and slightly cloudy solution. The small amount of impurity present appeared to be derived partly from the glass of the distillation flask, but the high figure obtained for sodium suggests that the reaction was not quite complete. The ease with which sodium ethoxide is acted on by moisture and carbon dioxide rendered it necessary to carry out all the operations in one vessel without admitting air, but it is then difficult to bring the substance into

thorough contact with the current of gas, as it adheres closely to the walls of the flask.

The results obtained with potassium ethoxide agree with those for the sodium compound, the product being in every case anhydrous potassium hydrosulphide. The slight coloration present in some of the sodium hydrosulphide preparations was either much fainter or absent altogether in the case of the corresponding products obtained from metallic potassium. The figures obtained on analysis of these products suggest a rather higher degree of purity for ordinary commercial metallic potassium than for metallic sodium.

Action of Hydrogen Sulphide on a Saturated Solution of Potassium Ethoxide.

2.2 Grams of metallic potassium were dissolved in 15 c.c. of absolute ethyl alcohol, and dry hydrogen sulphide was passed in until the solution was saturated. The crystalline product which separated was collected, sprayed with absolute alcohol, and dried in a vacuum. Unlike the corresponding product obtained from sodium, it was pure white. When examined microscopically it was seen to consist of very minute, but well defined, cubes. Weight of product = 1.93 grams:

0.2382 gave 0.2872 K_2SO_4 . $K = 54.04$.

KHS requires $K = 54.16$ per cent.

The filtrate was treated with 75 c.c. anhydrous ether, and the white, crystalline precipitate collected, washed, and dried in a vacuum:

0.3763 gave 0.4534 K_2SO_4 . $K = 54.01$.

0.2969 „ 0.9561 $BaSO_4$. $S = 44.22$.

KHS requires $K = 54.17$; $S = 44.44$ per cent.

Total yield of potassium hydrosulphide = 3.91 grams. Theory requires 4.04 grams. The properties of the substance are similar to those of the sodium compound, but it appears to be even more hygroscopic.

Action of Hydrogen Sulphide on Solid Potassium Ethoxide.

This reaction was carried out exactly as in the case of the sodium compound. Reaction took place immediately in the cold, and was more vigorous than with sodium ethoxide. The flask became hot, and a considerable quantity of alcohol distilled over. The product remaining after all the alcohol had been driven off possessed a very faint buff tint, and appeared more homogeneous

than the corresponding sodium compound. It dissolved in water and hydrochloric acid, giving clear solutions:

0.2122 gave 0.2535 K_2SO_4 . $K=53.55$.

0.1955 „ 0.6196 $BaSO_4$. $S=43.62$.

KHS requires $K=54.17$; $S=44.44$ per cent.

When the hydrosulphides are heated in the air they become yellow, and finally fuse to a dark red liquid. On cooling, a deep yellow solid is formed, which is soluble in water, giving a yellow solution, and is at once decomposed by hydrochloric acid, with vigorous evolution of hydrogen sulphide and precipitation of sulphur. Bloxam (*loc. cit.*) investigated the action of heat on potassium hydrosulphide, and determined its melting point, but there appear to be several matters in connexion with this action which require explanation, and further investigation is at present being carried out by the author.

The possibility of preparing the anhydrous monosulphides of sodium and potassium by the action of the hydrosulphides on the ethoxides in alcoholic solution, analogous to the ordinary preparation in aqueous solution, is obvious, and it is hoped to deal with this portion of the subject in a later paper.

In conclusion, I desire to thank Mr. J. Smeath Thomas, M.Sc., for kind assistance in connexion with this work.

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LXVII—*The Application of Viscometry to the Measurement of the Rate of Reaction.*

By ALBERT ERNEST DUNSTAN and ALBERT GEORGE MUSSELL.

SINCE the viscosity-coefficients of different substances vary between wide limits, it is possible to follow the course of a reaction, provided that there is sufficient variation in this property in the initial and final states. The application of physical methods to this end is already well known, and it will be sufficient briefly to notice the work of Patterson and McMillan in this direction. These authors (Trans., 1907, **91**, 504; 1908, **93**, 1041) took advantage of the fact that the rotation of ethyl tartrate is eminently sensitive to the presence of foreign substances. It varies largely, for example, when ethyl tartrate is dissolved in different solvents; and, conversely,

when an isodynamically changing compound is dissolved in this active liquid, the rotation changes in sympathy. In accordance with this, the above-mentioned authors measured the velocities of isodynamic change for benzsynaldoxime \rightarrow benzantialdoxime; piperonalsynoxime \rightarrow piperonalantioxime; ω -isonitrotoluene \rightarrow ω -nitrotoluene, and several similar cases. An important point brought out, which militates against the utility of this method for comparison purposes, is that the more highly purified ethyl tartrate afforded constants different from those given by the slightly less pure solvent, and, further, of course, the changing substance must be soluble in the ethyl tartrate.

The change of viscosity during a reaction has been used to follow the effect of heat on gelatin solutions (von Schroeder, *Zeitsch. physikal. Chem.*, 1903, **45**, 75). This author found $d\eta/dt = K((\eta_1 - \eta_2))$, where η_2 is the final value of the viscosity, so that if the total viscosity change be taken as a measure of the chemical change, it is obvious that a unimolecular reaction is here indicated. Beck, Trietsche, and Ebbinghaus (*Zeitsch. physikal. Chem.*, 1907, **58**, 425) also pointed out that change in viscosity might be utilised for the measurement of the velocity of a reaction.

In the present communication the authors have endeavoured to show that the viscometric method is applicable to a variety of chemical reactions, and probably to all, could the conditions be suitably governed. The following changes were found to be capable of measurement:

Freshly distilled acetoacetic ester (enolic) \rightarrow equilibrium mixture; aniline \rightarrow phenylthiocarbamide; ammonium thiocyanate \rightarrow thiocarbamide; ammonium cyanate \rightarrow carbamide; acetic anhydride \rightarrow acetic acid; benzoyl chloride \rightarrow benzoic acid; hydrolysis of benzsynaldoxime.

(1) *The Change of Viscosity of Freshly Distilled Ethyl Acetoacetate.*

Schaum (*Ber.*, 1898, **31**, 1964) first showed that acetoacetic ester underwent a change of density on keeping. He made the following determinations:

Fresh distilled.	Density, after 6 hours.	Density, after 24 hours.
1.0278	1.0282	1.0282
1.0278	1.0284	1.0284
1.0265	1.0269	1.0270

A more complete study of this change has been carried out for us by Mr. Thole, with the following results.

The ester was purchased from Kahlbaum. It boiled at $137^\circ/240$ mm. It was distilled at 6h. 25m. p.m.

Time h. m.	Density 25/4.	Viscosity.	$a - x$.	$\frac{1}{t} \cdot \log_e \frac{a}{a-x}$.
6 36	1.02094	—	—	—
6 42	—	0.015330	0.000063	—
6 49	1.02119	0.015340	0.000053	0.0246
7 6	1.02123	—	—	—
7 9	—	0.015367	0.000026	0.0327
7 15	—	0.015376	0.000017	0.0395
7 23	1.02125	—	—	—
7 35	—	0.015385	0.000008	0.0389
7 42	1.02128	—	—	—
7 48	—	0.015393	—	—
8 2	1.02128	—	—	—
8 50	1.02128	—	—	—
Average.....				0.0339

The densities required for this calculation of the viscosity-coefficients are interpolated from the curve drawn through the experimental points.

Considering the very small differences, the values of $\frac{1}{t} \cdot \log_e \frac{a}{a-x}$ are surprisingly constant.

(2) *Aniline Heated with Ammonium Thiocyanate to Form Phenylthiocarbamide.*

A hot saturated solution of ammonium thiocyanate was made in aniline. This was filtered into the viscometer heated to 130° in an oil-bath. Many experimental difficulties were met with, notably in the streams of bubbles evolved, which choked the capillary. The crude phenylthiocarbamide which separated on treating the reaction mixture with dilute hydrochloric acid melted at 149°.

Time (mins.).	Time of flow.	$a - x$.	$\frac{1}{t} \cdot \log_e \frac{a}{a-x}$.
0	177.2	—	—
4	171.2	5.8	0.177
7	168.6	3.2	0.186
11	167.0	1.6	0.161
15	165.6	0.2	0.211
19	165.4	—	—
Average.....			0.184

The probable cause of the reaction is the formation of thiocarbamide, which reacts with the large excess of aniline present to yield the phenyl derivative. In each case a unimolecular constant should be given.

(3) *Rate of Change of Ammonium Thiocyanate to Thiocarbamide.*

Attempts were made at first to follow this reaction by allowing the melted thiocyanate to remain for several hours in the viscometer, immersed in an oil-bath, the temperature of which was kept constant at about 160°. Insuperable difficulties were met with, however,

in the streams of bubbles which passed up through the capillary. Better results were obtained when the ammonium thiocyanate was heated in an oil-bath in a corked flask at a constant temperature. Samples were withdrawn every stated interval, and as they solidified immediately, it would be taken as certain that the reaction terminated at the time of removal of the sample.

One gram of the sample was dissolved in 12 c.c. of water, and the viscosity determined immediately after filtration into the viscometer.

Temperature of oil-bath 160° . One gram of product dissolved in 12 c.c. of water.

Time of withdrawal (in hours).	Time of flow (in seconds).
0	230.0
1	231.5
2	233.0
4	235.0
7	236.0
11.5	236.1*
Pure thiocarbamide.....	248.0
Thiocarbamide heated 1 hour	240.0
„ „ 3½ hours ...	236.0

* Part of product was insoluble, and odour of hydrogen sulphide was observed.

When these results are plotted, it is found that they lie on two curves which approach each other. The viscosity at equilibrium is 236, and this corresponds with an equilibrium mixture of 33 per cent. of thiocarbamide.

Polarimetrically, Patterson and McMillan (*loc. cit.*) obtain 45 per cent., whilst Werner and Reynolds (*Trans.*, 1903, **83**, 1) found 24.72 per cent. (at temperatures between 170° and 180°).

(4) *Rate of Change of Ammonium Cyanate into Carbamide.*

Very many experiments have been made on the measurement of this reaction. It has been found best to mix two cold equivalent saturated solutions of ammonium sulphate and potassium cyanate, filter off the precipitated potassium sulphate, and, on cooling, further to filter the solution of ammonium cyanate into the viscometer. At the ordinary temperature (25°) the reaction proceeds slowly, yet measurably. A typical series is given below.

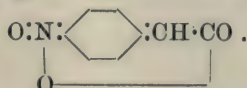
Solution made at 9.40 a.m.

Time (mins.).	Time of observation.	Time of flow.	$a - x$.	$\frac{1}{t} \cdot \log_{10} \frac{a}{a-x}$.
0	Wednesday 10.10 a.m.	4'29"	36.0	—
50	" 11.0 "	4'30"	35.0	0.00024
120	" 12.10 p.m.	4'32"	33.0	0.00031
238	" 2.8 "	4'34.6"	30.4	0.00031
247	" 2.17 "	4'35.0"	30.0	0.00032
290	" 3.0 "	4'36.0"	29.0	0.00032
350	" 4.0 "	4'38.0"	26.7	0.00037
560	" 7.30 "	4'45.0"	20.0	0.00045
Following Saturday...	12.30 "	5'5.0"	—	—

These values for K sufficiently confirm the experimental work of Patterson (*loc. cit.*), Walker, Hambly, Kay, and Wood (Trans., 1895, **67**, 746; 1897, **71**, 489; 1898, **73**, 21) that this reaction is not of the first order.

(5) Effect of Alkali on p-Nitrophenylacetonitrile.

We are indebted to Mr. F. G. Pope, of East London College, for a supply of the above compound. On being dissolved in absolute alcohol, it gives a colourless solution, which, with a little alcoholic potassium hydroxide, turns to red. After several hours it darkens considerably, and on pouring into water, becomes emerald-green. It is possible that hydrolysis of the nitrile group goes on, followed by intramolecular change to a substance of the formula:



A saturated solution was made in ethyl alcohol, to which was added a few drops of alcoholic sodium hydroxide. The times of flow were plotted against times of observation, and a regular curve drawn through. The following results were obtained from interpolated values:

Time (mins.).	$a - x$ (in $\frac{1}{2}$ seconds).	$\frac{1}{t} \cdot \log_{10} \frac{a}{a-x}$.
0	63	—
5	41	0.0373
10	32	0.0294
15	25	0.0267
20	18	0.0272
25	15	0.0249
30	11	0.0252
35	9	0.0241
40	6	0.0255

Average..... 0.0288

The reaction apparently tends to the first order after the first ten minutes.

(6) *The Hydration of Acetic Anhydride in Acetic Acid Solution.*

Many preliminary experiments have been carried out with the intention of studying the rate of hydration of acetic anhydride with the equivalent weight of water, both dissolved in pure acetic acid. As we are still working on this reaction, one set only will be here quoted.

5 c.c. acetic acid (frozen out repeatedly).
4.72 c.c. acetic anhydride (b. p. 135°/739 mm.). 0.90 c.c. of water.

Time (mins.).	Time of flow (secs.).	$a - x$.	$\frac{1}{t} \cdot \log_{10} \frac{a}{a-x}$.
0	158.0	6.6	—
15	159.0	5.6	0.0048
22	159.6	5.0	0.0054
37	160.4	4.2	0.0053
45	161.2	3.4	0.0064
52	161.4	3.2	0.0060
65	164.0	2.6	0.0062
115	164.6	—	—
Average			0.00568

Our experiments indicate that the above reaction is by no means so simple as might be supposed, for at some concentrations the velocities of efflux become less as time goes on, whilst the absolute viscosities may rise to a maximum, and then steadily fall. This is shown in the accompanying table.

5 c.c. of acetic acid.
4.72 c.c. of acetic anhydride. 0.45 c.c. of water.

Time.	Viscosity.	Time.	Viscosity.
12.22 p.m.	0.01370	4.32 p.m.	0.01379
12.31 „	0.01374	6.26 „	0.01368
12.44 „	0.01377	7.8 „	0.01365
12.57 „	0.01383	7.54 „	0.01362
3.12 „	0.01395	9.5 „	0.01353
4.14 „	0.01396	9.35 „	0.01352

(7) *The Hydrolysis of Benzoyl Chloride in Aqueous Acetone.*

Benzoyl chloride being not sufficiently soluble in water, a solution in aqueous acetone was made up of the following molecular concentrations: acetone, 100; water, 203.4; benzoyl chloride, 5.2.

Time (mins.).	Time of flow.	$\frac{1}{t} \cdot \log_e \frac{a}{a-x}$.
11.5	406.2	—
14.5	412.2	0.00952
22.5	425.4	0.01025
44.5	441.0	0.00954
53.0	444.2	0.00956
80.0	448.0	0.01030
140.0	449.0	—
Average		0.00983

Interpolated from curve:

19.3	—	0.00954
34.0	—	0.00954
64.0	—	0.00956

The benzoyl chloride was recovered in the form of benzoic acid at the end of the experiment.

We have also made a number of experiments with the *syn*-oximes. We hoped to follow the transformation of these substances into their *anti*-isomerides, but up to the present have found no means of inducing the change. *Benzsynaldoxime*, for example, is a very stable compound. It can be crystallised unchanged from hot alcohol, benzene, or amyl acetate, or even from hot water, so that our expectation that it would be converted into the *anti*-aldoxime in solution was not realised.

In conclusion, we wish to thank Mr. A. S. Wood and Mr. A. Perry for their assistance with the experiments on the oximes and benzoyl chloride respectively.

PHYSICAL CHEMICAL LABORATORY,
EAST HAM TECHNICAL COLLEGE.

LXVIII.—*Synthesis of Dipeptides of α -Aminolauric Acid with Glycine, Alanine, Valine, Leucine, and Asparagine.*

By ARTHUR HOPWOOD and CHARLES WEIZMANN.

IN view of the possible presence of peptides of α -aminolauric acid with amino-acids in the products of hydrolysis occurring in certain plants, the authors have prepared the dipeptides of α -aminolauric acid with glycine and other amino-acids, so that they may be compared with the products obtained by the hydrolysis of proteins contained in *Laurus nobilis*, pichurum beans, and other proteins. From another point of view the peptides derived from higher fatty acids are of considerable interest, since a study of their properties may throw some light on the lipoproteins and the transformation of proteins proper into lipoproteins, a process probably taking place in the fatty degeneration of the cell (Bondi and Frankl, *Biochem. Zeitsch.*, 1909, 17, 543).

EXPERIMENTAL.

The method of synthesis adopted was one which has been so successfully used by Emil Fischer (*Ber.*, 1903, **36**, 2982 *et seq.*) in the synthesis of polypeptides containing the radicles of the lower members of the series of fatty acids. In brief, the method consists in condensing α -bromolauryl chloride with amino-acids in presence of sodium hydroxide, and then displacing the halogen in the product by an amino-group through the action of ammonia.

 α -Bromolauryl Chloride, $C_{11}H_{22}Br \cdot COCl$.

One hundred grams of phosphorus pentachloride (1 mol.) are added gradually, with vigorous shaking, to 134 grams of α -bromolauric acid (1 mol.), and, after the energetic action has subsided, the mixture is heated on a water-bath for an hour. The product is distilled under diminished pressure, and the fraction boiling at $150\text{--}175^\circ/16$ mm. is collected. Yield, 95 grams:

0.3010 gave $AgCl + AgBr = 0.3380$.

$C_{12}H_{22}OBrCl$ requires $AgCl + AgBr = 0.3351$ per cent.

α -Bromolauryl chloride is a colourless liquid, which boils at $150^\circ/10$ mm., and at $170^\circ/16$ mm. It has a pungent odour, and is decomposed slowly by water.

 α -Bromolaurylglycine, $C_{11}H_{22}Br \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$.

Forty grams of α -bromolauryl chloride (1 mol.) and an aqueous solution containing 5 grams of sodium hydroxide (1 mol.) are added gradually and alternately, with frequent shaking, to an aqueous solution containing 10 grams of glycine (1 mol.) and 5 grams of sodium hydroxide (1 mol.). The solution is heated on a water-bath until the odour of α -bromolauryl chloride disappears, then allowed to cool, and dilute hydrochloric acid added in slight excess. A colourless precipitate of impure α -bromolaurylglycine separates out, which is allowed to remain for several hours, then collected, washed with cold water, and dried in air on a porous plate. Yield, 43 grams. The product crystallises from benzene in colourless, rhombic plates, which melt at $117\text{--}118.5^\circ$. The crystals are only sparingly soluble in water, but readily so in alcohol, ether, benzene, toluene, or alkalis:

0.1627 gave 0.0921 $AgBr$. $Br = 24.09$.

$C_{14}H_{26}O_3NBr$ requires $Br = 23.78$ per cent.

 α -Aminolaurylglycine, $NH_2 \cdot C_{11}H_{22} \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$.

Five grams of α -bromolaurylglycine are mixed with excess of strong aqueous ammonia, and the mixture heated at 100° for an

hour. On evaporating the solution until the excess of ammonia is expelled, colourless crystals are obtained, from which water is removed by adding absolute alcohol, and then evaporating to dryness on a water-bath. In order to remove the ammonium bromide and unchanged α -bromolaurylglycine, the dry residue is boiled with absolute alcohol, and then collected, when 3 grams of nearly pure α -aminolaurylglycine are obtained. For further purification, the dipeptide is dissolved in absolute alcohol containing a little aqueous ammonia, filtered, and the filtrate boiled until the ammonia disappears, when the pure peptide separates out, and is collected, washed with absolute alcohol, and dried in air on a porous plate. It forms prismatic needles, which sinter at 207° , and melt and decompose at $214\text{--}214.5^{\circ}$:

0.1975 gave 0.4475 CO_2 and 0.1858 H_2O . $\text{C}=61.79$; $\text{H}=10.52$.

0.2059 „ 18.7 c.c. N_2 at 19.0° and 757.6 mm. $\text{N}=10.58$.

$\text{C}_{14}\text{H}_{28}\text{O}_3\text{N}_2$ requires $\text{C}=61.70$; $\text{H}=10.36$; $\text{N}=10.29$ per cent.

The dipeptide is almost insoluble in water, sparingly soluble in alcohol, but readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it gives a white, amorphous precipitate with aqueous phosphotungstic acid, which, as in the case of the proteins, is soluble in excess of the reagent. In presence of alkali hydroxide, the dipeptide condenses with β -naphthalenesulphonyl chloride, yielding β -naphthalenesulphonyl-aminolaurylglycine, which crystallises from much water in colourless, rhombic plates, melting and decomposing at $205\text{--}207^{\circ}$.

α -Bromolaurylalanine, $\text{C}_{11}\text{H}_{22}\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$.

Ten grams of α -bromolauryl chloride (1 mol.) and 34 c.c. of *N*-sodium hydroxide (1 mol.) are added gradually and alternately, with frequent shaking, to a solution containing 3 grams of alanine (1 mol.) in 34 c.c. of *N*-sodium hydroxide (1 mol.). The solution is heated on a water-bath until the odour of α -bromolauryl chloride disappears, then allowed to cool, and dilute hydrochloric acid added in slight excess. A curdy, colourless precipitate of impure α -bromolaurylalanine separates out, which is kept for several days, then collected, washed with water, and dried. Yield, 9.6 grams. The product crystallises from benzene in colourless, rhombic plates, which melt very sluggishly at $104\text{--}116^{\circ}$, probably indicating a mixture of two stereoisomeric α -bromolaurylalanines. The crystals are sparingly soluble in hot water, moderately so in dilute alcohol, and readily so in absolute alcohol, ether, benzene, toluene, or alkalis:

0.1232 gave 0.0670 AgBr . $\text{Br}=23.15$.

$\text{C}_{15}\text{H}_{28}\text{O}_3\text{NBr}$ requires $\text{Br}=22.82$ per cent.

α -Aminolaurylalanine, $\text{NH}_2 \cdot \text{C}_{11}\text{H}_{22} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$.

Five grams of α -bromolaurylalanine, when treated with aqueous ammonia in the same way as α -bromolaurylglycine, yield 2.9 grams of *α -aminolaurylalanine*, which crystallises from alcohol in prismatic needles, melting and decomposing at 212 – 213° . The dipeptide is sparingly soluble in water, moderately so in alcohol, and readily so in ammonia, alkali hydroxides, or mineral acids. A white, amorphous precipitate is produced when an aqueous solution of phosphotungstic acid is added to a solution of the dipeptide in dilute sulphuric acid:

0.1518 gave 0.3493 CO_2 and 0.1451 H_2O . $\text{C} = 62.75$; $\text{H} = 10.69$.

0.1173 „ 9.9 c.c. N_2 at 18.0° and 769.3 mm. $\text{N} = 10.02$.

$\text{C}_{15}\text{H}_{30}\text{O}_3\text{N}_2$ requires $\text{C} = 62.88$; $\text{H} = 10.56$; $\text{N} = 9.79$ per cent.

 α -Bromolaurylvaline, $\text{C}_{11}\text{H}_{22}\text{Br} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMe}_2$.

Ten grams of α -bromolauryl chloride are condensed, as described for α -bromolaurylalanine, with 4 grams of valine. The yield of impure *α -bromolaurylvaline* is 9.0 grams. The product crystallises from benzene in small, rhombic plates, which melt at 137 – 140° . The crystals are sparingly soluble in hot water, readily so in dilute or absolute alcohol, ether, benzene, toluene, or alkalis:

0.2484 gave 0.1214 AgBr . $\text{Br} = 20.80$.

$\text{C}_{17}\text{H}_{32}\text{O}_3\text{NBr}$ requires $\text{Br} = 21.13$ per cent.

 α -Aminolaurylvaline, $\text{NH}_2 \cdot \text{C}_{11}\text{H}_{22} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMe}_2$.

Five grams of α -bromolaurylvaline, when treated with aqueous ammonia in the same way as α -bromolaurylglycine, yield 3.5 grams of *α -aminolaurylvaline*, which crystallises from alcohol in small, rhombic plates, sintering at 205° , and melting and decomposing at 212 – 214° . The dipeptide is almost insoluble in water, sparingly soluble in alcohol, and readily so in ammonia, alkali hydroxides, or mineral acids. A white, amorphous precipitate is produced when an aqueous solution of phosphotungstic acid is added to a solution of the dipeptide in dilute sulphuric acid:

0.1185 gave 0.2818 CO_2 and 0.1162 H_2O . $\text{C} = 64.83$; $\text{H} = 10.97$.

0.1236 „ 9.6 c.c. N_2 at 18.5° and 772.3 mm. $\text{N} = 9.24$.

$\text{C}_{17}\text{H}_{34}\text{O}_3\text{N}_2$ requires $\text{C} = 64.91$; $\text{H} = 10.90$; $\text{N} = 8.92$ per cent.

 α -Bromolauryl-leucine, $\text{C}_{11}\text{H}_{22}\text{Br} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CHMe}_2$.

Ten grams of α -bromolauryl chloride are condensed, as described for α -bromolaurylalanine, with 4.4 grams of *r*-leucine. The yield

of impure α -bromolauryl-leucine is 10.5 grams. The product crystallises from dilute alcohol in large, colourless, prismatic plates, and from benzene in colourless, rhombic plates, melting at 128—131°. The crystals are sparingly soluble in water, moderately so in dilute alcohol, and readily so in absolute alcohol, acetone, ethyl acetate, benzene, or alkalis:

0.1018 gave 0.0493 AgBr. Br = 20.61.

$C_{18}H_{34}O_3NBr$ requires Br = 20.37 per cent.

α -Aminolauryl-leucine, $NH_2 \cdot C_{11}H_{22} \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CHMe_2$.

Five grams of α -bromolauryl-leucine, when treated with aqueous ammonia in the same way as α -bromolaurylglycine, yield 3.0 grams of *α -aminolauryl-leucine*, which crystallises from alcohol in stout prisms melting and decomposing at 223.5—225.5°. The dipeptide is sparingly soluble in water, moderately so in alcohol, and readily so in ammonia, alkali hydroxides, or mineral acids. A white, amorphous precipitate is produced when an aqueous solution of phosphotungstic acid is added to a solution of the dipeptide in dilute sulphuric acid:

0.1018 gave 0.2465 CO_2 and 0.1014 H_2O . C = 66.04; H = 11.14.

0.2344 „ 16.7 c.c. N_2 at 19.5° and 768.1 mm. N = 8.41.

$C_{18}H_{36}O_3N_2$ requires C = 65.80; H = 11.05; N = 8.53 per cent.

α -Bromolaurylasparagine,

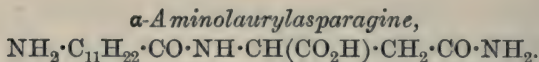
$C_{11}H_{22}Br \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CO \cdot NH_2$.

Five grams of *l*-asparagine (1 mol.) are dissolved in 33.5 c.c. of *N*-sodium hydroxide (1 mol.), and then a further quantity of 33.5 c.c. of *N*-sodium hydroxide (1 mol.) and 9.92 grams of α -bromolauryl chloride are added gradually and alternately with vigorous shaking. The temperature is kept at about 15° by cold water. On adding a slight excess of dilute hydrochloric acid to the clear solution, a pale yellow precipitate of impure α -bromolaurylasparagine separates out, which is collected, washed with water, and dried. Yield, 12 grams. On crystallising the product from absolute alcohol, a mixture of colourless, rhombic plates and long, prismatic needles is obtained; these melt and decompose at 148—150°. The crystals are only sparingly soluble in water or benzene, but readily so in dilute or absolute alcohol, ammonia, or alkali hydroxides:

0.1889 gave 11.6 c.c. N_2 at 19.5° and 779.2 mm. N = 7.35.

0.1650 „ 0.0786 AgBr. Br = 20.27.

$C_{16}H_{29}O_4N_2Br$ requires N = 7.13; Br = 20.32 per cent.



Five grams of α -bromolaurylasparagine, when treated with aqueous ammonia in the same way as α -bromolaurylglycine, yield 2.5 grams of *α -aminolaurylasparagine*, which crystallises from absolute alcohol in colourless, rhombic plates, melting and decomposing at 242.0 — 243.5° . The dipeptide is sparingly soluble in water or alcohol, but readily so in ammonia, alkali hydroxides, or mineral acids. A white, amorphous precipitate is produced when an aqueous solution of phosphotungstic acid is added to a solution of the dipeptide in dilute sulphuric acid:

0.1135 gave 0.2415 CO_2 and 0.0970 H_2O . $\text{C} = 58.02$; $\text{H} = 9.56$.

0.1206 „ 13.0 c.c. N_2 at 18.0° and 778.2 mm. $\text{N} = 12.95$.

$\text{C}_{16}\text{H}_{31}\text{O}_4\text{N}_3$ requires $\text{C} = 58.30$; $\text{H} = 9.49$; $\text{N} = 12.77$ per cent.

Action of Enzymes on the Dipeptides.

Pancreatic juice activated by kinase, pancreatine (Defresne), trypsin (Merck), muscle juice, or liver extract hydrolyse α -aminolaurylglycine, but papayotine (Merck) is without action.

Micro-organisms develop slowly on ordinary artificial media containing α -aminolaurylglycine as the sole source of nitrogen. The feeble growth of micro-organisms can be ascribed to the sparing solubility of the peptides in aqueous solutions of the media. If *B. Subtilis*, *B. Pyocyaneus*, or *Proteus vulgaris* are cultivated on dilute solutions of peptone rendered slightly alkaline with potassium carbonate and saturated with α -aminolaurylglycine, a decomposition of the peptide is observed after twenty-four hours.

In carrying out these biological tests, considerable assistance was afforded us by Dr. Berthelot, of the Pasteur Institute.

THE UNIVERSITY,
MANCHESTER.

ANNUAL GENERAL MEETING,

MARCH 23RD, 1911.

Prof. HAROLD B. DIXON, M.A., Ph.D., F.R.S., in the Chair.

Dr. J. E. MACKENZIE and Dr. R. H. ADERS PLIMMER were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society during the past twelve months; and the TREASURER made his statement as to the Society's Income and Expenditure for 1910. After some remarks by Dr. G. McGowan, Mr. A. W. Oke, and Dr. J. A. Voelcker, the Adoption of the Report of the Council, together with the Balance Sheet and Statements of Accounts for the year ended December 31st, 1910, proposed by Mr. DAVID HOWARD and seconded by Dr. F. B. POWER, was carried unanimously.

A Vote of Thanks to the Auditors was proposed by the TREASURER, seconded by Dr. S. SMILES, and acknowledged by Dr. V. H. VELEY.

REPORT OF THE COUNCIL.

Since our last Anniversary Meeting, we, in common with the rest of the Empire, have had to deplore the loss of the gracious Sovereign whose mission of peace among the nations did so much to foster the steady growth of science. In the address of condolence and of loyalty to his throne which his Majesty King George V. was pleased to receive from the Chemical Society, the Council ventured to call to mind, not only our indebtedness to his late Majesty, but also how much the progress of chemistry in Great Britain was due to the wisdom and foresight of the Prince Consort in the early days of the Society.

The Council is again in a position to report favourably on the progress of the Society, as indicated by an increase in the number of Fellows, and in the list of papers communicated.

On the 31st December, 1909, the number of Fellows was 3,003. During 1910, 165 Fellows have been elected, and 5 were reinstated, the gross total thus being 3,173. The Society has lost 18 Fellows by death; 38 have resigned; the election of 1 Fellow has become void, and 43 Fellows have had their names removed from the list of Fellows for non-payment of annual subscriptions.

The total number of Fellows, therefore, at the 31st December, 1910, was 3,073, showing a net increase of 70 over the preceding year.

The names of the deceased Fellows, with the dates of their election, are:

Richard Abegg (1906).	Edwin Bernard Hadley (1898).
Robert Barklie (1870).	Angus Mackay (1877).
Robert Haslam Durward Benn, (1904).	Sir Walter Palmer, Bart. (1879).
Thomas Blackburn (1886).	Arthur Gaved Phillips (1887).
James Campbell Brown (1867).	Richard Wightwick Roberts (1889).
Benjamin Samuel Bull (1898).	Thomas Bertram Udall (1876).
Michael Carteighe (1864).	John Tsawoo White (1889).
John Croysdale (1895).	Charles Hanson Greville Williams (1862).
Frank Barnes Grundy (1903).	
Oscar Guttman (1897).	

The following Fellows have resigned:

John Charles Aylan.	Leonard Edward Beard Pearse.
Frederick Nolan Baker.	Geoffrey Surtees Phillpotts.
Frederic Edmund Bowman.	William Edmund Francis Powney.
Frank Curzon Britten.	Franklin Ernest Robertson.
William Burton.	Christopher Foulis Roundell.
Edward Henry Croghan.	Edward Cox Seaton.
*Frank Rawlinson Dudderidge.	Leonard Smith.
Alexander Esilmann.	Alec. Bowring Steven.
*William French.	Edward Stokes.
Gilbert Prout Girdwood.	Leonard Sumner.
Alfred George Cooper Gwyer.	Richard Noel Garrod Thomas.
Frederick John Hambly.	George Malcolm Thomson.
Arthur Lonsdale Hetherington.	John Booty Tillott.
Philip Holland.	William Gaylord Tucker.
John Atkinson Jennings.	James Neill Watts.
Harry Lancelot Lee.	James Scott Wilson.
Lionel Ludlow.	Lewis Thompson Wright.
George Harry Major.	John William Young.
Hubert Fredk. Sankey Marshall.	Thomas Arthur Young.

The names of the Fellows, reinstated by the Council in accordance with Bye-Law IV., are as follows:

Edwin Bayles Atkinson.
 Frank Rawlinson Dudderidge.
 William French.
 Percy Walter Jones.
 Charles Frederic Townsend.

* Since reinstated.

The number of Honorary and Foreign Members at the end of 1909 was 33. The Society has to mourn the loss of Professor Stanislao Cannizzaro, Professor Dr. Rudolf Fittig, and Geheim Rath Professor Dr. Hans Landolt, who died during 1910.

It is with great pleasure that the Council offers its congratulations to the following gentlemen, who, during the past year, attained their Jubilee as Fellows of the Society:

Professor Edward Divers, F.R.S.

Mr. Francis Sutton.

Mr. Charles Henry Wood.

During the year 1910, 349 scientific communications have been made to the Society, 273 of which have been published already in the Transactions, and abstracts of all have appeared in the Proceedings.

The volume of Transactions for 1910 contains 2,652 pages, of which 2,601 are occupied by 270 memoirs, the remaining 51 pages being devoted to the Obituary Notices, the Thomsen Memorial Lecture, the Report of the International Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 236 memoirs, which occupy 2,133 pages.

The Journal for 1910 contains 4,867 abstracts, which extend to 2,032 pages, whilst the abstracts for 1909 numbered 4,946, and occupied 2,040 pages. The abstracts may be classified as follows:

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	908	1,634

PART II.

General and Physical Chemistry		961
Inorganic Chemistry		494
Mineralogical Chemistry		118
Physiological Chemistry		700
Chemistry of Vegetable Physiology and Agriculture		287
Analytical Chemistry		673
	1,124	3,233
<hr/>		
Total in Parts I. and II.	2,032	4,867

During the past year the Society has rejoiced in having the

privilege of offering its congratulations and those of the whole chemical world to five of its Past Presidents, who had completed upwards of fifty years' Fellowship of the Society, namely, Prof. W. Odling, the Right Hon. Sir Henry E. Roscoe, Sir William Crookes, Dr. Hugo Müller, and Dr. A. G. Vernon Harcourt. The Banquet held on Friday, November 11th, 1910, to do honour to these gentlemen will remain a notable event in the history of the Chemical Society. To the great regret of all, Sir Henry Roscoe was, owing to indisposition, unable to be present.

In order to render more complete the records and statistics of the Society, and to make them available to the Fellows at large, the Council has ordered the preparation of a complete chronological list of Fellows from the foundation of the Society in 1841.

Professor Theodore W. Richards has been invited to deliver the Faraday Lecture, and the Council has pleasure in announcing that, through the courtesy of the Managers, an extraordinary meeting of the Society will be held on June 14th in the Lecture Theatre of the Royal Institution, where all the Faraday Lectures have been given. The title of the discourse will be announced in due course.

On behalf of the Society, the Council presented a Congratulatory Address to its Honorary and Foreign Member, Professor Wilhelm Körner, on the occasion of his seventieth birthday.

By the death of Stanislaw Cannizzaro, the Society has lost its Senior Honorary and Foreign Member, elected on June 19th, 1862. Sir William Tilden has accepted the invitation of the Council to deliver a Memorial Lecture in his honour.

The Council has further arranged for the following Memorial Lectures to be delivered:

Antoine Henri Becquerel (d. Aug. 25th, 1908). By Professor Ernest Rutherford, F.R.S.

Marcellin Berthelot (d. March 18th, 1907). By Professor Harold B. Dixon, F.R.S.

Henri Moissan (d. Feb. 20th, 1907). By Sir William Ramsay, K.C.B., F.R.S.

In response to an appeal from the University of Toulouse for help in attempting to render good the almost complete destruction of the Science portion of its library by fire on October 27th last, the Council have decided to present the University with a number of volumes of the Transactions of the Chemical Society. It is unfortunately impossible for the Society on such an occasion as this to present a complete set of its publications, owing to the fact that many of the earlier volumes are out of print.

A number of volumes of the Transactions has also been presented to the University of Manitoba, Winnipeg.

In December, 1909, the International Commission for the publication of Physical-Chemical Constants invited the Society to assist in the work of the Commission by contributing towards the expenses of its work. After due consideration, the Council has decided to make a contribution of £10 out of the funds of the Society for the year 1911, at the expiry of which time the matter will receive further consideration.

An intimation has been received from the Secretary of the International Congress of Applied Chemistry that the Congress will meet in the first half of the month of September, 1912, the opening meeting to be held in Washington, and subsequent meetings of the Congress and its Sections in New York City.

Professor A. Haller, on behalf of the Chemical Society of France, has invited the Chemical Society to co-operate in the formation of an International Committee to consider questions of chemical nomenclature and other matters, with a view to facilitate the reading of chemical researches published in different languages. Professor Haller suggests that established Chemical Societies should appoint delegates to meet once or twice a year, and that questions considered at such meetings should be referred to and discussed by the several Societies independently, and then finally by the International Committee.

The Council has expressed its willingness to appoint delegates to serve on the International Committee, should such be formed.

The Chemical Society has during the past year received, through the kindness of Professor G. Carey Foster, a copy of Richard Watson's "*Pars Metallurgica Institutium Chemicarum*"; the Right Hon. Sir Henry E. Roscoe has presented a unique set of photograph portraits of Chevreul; and Mr. Ernest de la Rue has added to the collection of portraits one of the late Warren de la Rue, who was President of the Society during two periods, 1867-1869 and 1879-1880. Valuable presents of the Society's publications have also been received from Mr. J. McDougall and Dr. E. Cox Seaton.

During the year, 1,918 books were borrowed from the Library, as against 1,548 during 1909; of these, 553 were issued by post, as compared with 347 in the preceding year.

The additions to the Library comprise: 163 books, of which 80 were presented, 431 volumes of periodicals (representing 236 journals), and 141 pamphlets, as against 142 books, 418 volumes of periodicals (representing 243 journals), and 80 pamphlets last year.

Although the income of the Society for the year 1910 falls short of its expenditure by no less than £147 6s. 4d., this need hardly cause any serious alarm, nor must it be assumed that henceforth

INCOME AND EXPENDITURE ACCOUNT

		<i>Income.</i>			
		£	s. d.	£	s. d.
To Life Compositions				219	0 0
„ Admission Fees				636	0 0
„ Annual Subscriptions—					
Received in advance, on account of 1910		287	0 0		
„ during 1910		4183	0 0		
„ „ „ 1909		340	0 0		
„ „ „ 1905-8		14	0 0		
		4804	0 0		
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet		356	0 0		
		4448	0 0		
Add Arrears at date: 1910 £468; 1909 £14; 1908 £2, estimated to realise as per Balance Sheet		370	0 0		
				4818	0 0
„ Lady Subscribers				3	0 0
„ Investments:—					
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...		221	16 4		
„ £1050 London and North Western Railway 3 per cent. Debenture Stock		29	13 2		
„ £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock ...		42	19 4		
„ £1400 India 2½ per cent. Stock		32	19 4		
„ £2400 Bristol Corporation 2½ per cent. Debenture Stock ...		56	10 0		
„ £4341 Midland Railway 2½ per cent. Preference Stock ...		102	3 10		
„ £1200 Leeds Corporation 3 per cent. Stock		33	18 0		
„ £1500 Transvaal 3 per cent. Guaranteed Stock		42	7 6		
„ £1200 North British Railway 3 per cent. Debenture Stock		33	18 0		
„ £700 Canada 3½ per cent. Stock 1930/50		11	10 8		
„ Income Tax Recovered		30	2 0		
„ Interest on Deposit Account		12	6 5		
				650	4 7
Publications:—					
Sales:					
Journals		877	15 6		
Proceedings		29	1 8		
General Index		19	17 4		
Library Catalogue		1	1 9		
Atomic Weight Tables		1	0 8		
Annual Reports on the Progress of Chemistry		140	7 0		
		1069	3 11		
Less Publishers' Commission		102	18 9		
		966	5 2		
Proceeds of Advertisements in Journal... ..	£125 4 1				
Less Commission	4 10 3				
		120	13 10		
				1086	19 0
„ Sale of Waste Paper				1	0 9
„ Subscriptions from other Societies:—					
Society of Chemical Industry		9	9 0		
Society of Public Analysts		11	0 6		
Faraday Society		2	2 0		
Optical Society		8	18 6		
Optical Convention		1	11 6		
				38	1 6
„ Balance, being excess of Expenditure over Income, carried to Balance Sheet				147	6 4
				£7594	12 2

I have examined the above Accounts with the Books and Vouchers of the Society, and the Investments

FOR THE YEAR ENDED 31ST DECEMBER, 1910.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal and Proceedings:—						
Salary of Editor, including Indexing	570	0	0			
Salary of Sub-Editor	200	0	0			
Editorial Postages	24	2	5			
Abstractors' Fees	485	5	10			
Printing of Journal	2879	7	11			
Banding	62	3	2			
Printing of Advertisements	45	1	5			
Wrappers and Addressing	115	10	9			
Distribution of Journal	597	2	8			
Authors' Copies	191	13	6			
Insurance of Stock at Clay's	7	0	0			
				5177	7	8
Printing of Proceedings	223	12	8			
Banding „	7	8	1			
Distribution „	35	3	1			
				266	3	10
„ Annual Reports on the Progress of Chemistry				429	10	1
„ Purchase of back numbers of Journal				5	10	3
„ List of Fellows				64	7	2
„ Library Expenses:—						
Salary of Librarian and Assistant... ..	170	8	0			
Books and Periodicals	244	4	3			
Binding	67	1	7			
				481	13	10
„ Indexing for International Catalogue				30	0	0
„ Balance of Dinner Account				91	15	2
„ Administrative Expenses:—						
Salary of Assistant Secretary	270	0	0			
Salary of Office Assistant... ..	46	16	8			
Wages (Commissionaire, Housekeeper, and Charwoman)	164	19	6			
Pension, Mrs. Hall	22	10	0			
Coal and Lighting	39	10	7			
House Expenses and Repairs	144	0	4			
Tea Expenses	27	15	1			
Insurances	9	13	10			
Accountants' Charges, 1910	21	0	0			
Commission on Recovery of Income Tax	1	10	1			
Printing	96	11	8			
Stationery	64	8	9			
Illuminated Addresses	5	18	0			
Postages... ..	105	8	1			
Valuation of Furniture	4	4	0			
Miscellaneous Expenses	23	17	6			
				1048	4	1

£7594 12 2

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved—

VICTOR H. VELEY,
FREDERICK B. POWER.
JOHN M. THOMSON.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance	308	10	0
„ Cash received on Account of Annual Report, Vol. VII. (not published)	30	18	6
„ Sundry Creditors	1589	7	5
„ Research Fund:— As per last Balance Sheet	10475	15	4			
Add Excess of Income over Expenditure for the year	29	6	5	10505	1	9
				12483	17	8
„ Chemical Society: Excess of Assets over Liabilities:— As per last Balance Sheet...	20304	16	5			
Less Excess of Expenditure over Income for the year	147	6	4	20157	10	1

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):— £6730 Metropolitan Consolidated 3½ per cent. Stock	7212	8	6			
£1090 London and North Western Railway 3 per cent. Debenture Stock	839	12	0			
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India 2½ per cent. Stock	1316	1	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock...	1460	13	6			
£1200 North British Railway 3 per cent. Debenture-Stock	1033	11	0			
£700 Canada 3½ per cent. Stock, 1930/50	704	8	6			
				21001	19	11

(Estimated present value of Investments,

£18553 16s. 3d.

„ Sundry Debtors:—

Optical Society	8	18	6
Advertising Accounts	62	15	3
Messrs. Gurney & Jackson	426	15	5
Telephone Deposit	1	0	0
„ Subscriptions in Arrear, £484. Estimated to realise ..				499	9	2
„ Insurance paid in advance	370	0	0
„ Cash at Bank on Current Account	66	17	1
„ Cash in hand	11	2	11
				147	19	10

„ Research Fund:—

Investments (value when acquired):

£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587	18	0
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049	15	11
£1142 10s. New South Wales 3 per cent. Stock	1000	0	0
£1122 Metropolitan Water Board 3 per cent. „B” Stock	1002	16	9
£1365 Midland Railway 2½ per cent. Debenture Stock	1010	0	9
£806 Victoria 3 per cent. Stock	706	6	2
	10366	17	7

(Estimated present value of Research

Fund Investments, £9769 6s. 11d.)

„ Cash at Bank	138	4	2
				10505	1	9

NOTE.—The estimated value of the Library, exclusive of the Stock of the Society's own publications, is £7200, and of the Furniture, &c., £3350.

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1910.

ANNUAL GENERAL MEETING.

Income.		Expenditure.	
£	s. d.	£	s. d.
To Dividends on :—			
£1000 North British Railway 4 per cent. No. 1 Preference Stock			
37	13 4	Brought forward—180	
145	0 4	H. Browning, jun.	
24	6 10	A. Clayton	
32	5 10	W. W. Close	
31	14 0	J. B. Cohen	
32	2 8	C. H. Desch	
22	15 4	J. G. M. Dunlop	
		F. P. Dunn	
		A. E. Dunstan	
		J. Ferns	
		W. Godden	
		V. J. Harding	
		W. N. Haworth	
		A. Holt, jun.	
		F. Holt	
		E. Hope	
		W. J. Jarrard	
		F. R. Lankshear	
		A. Lapworth	
		H. R. Le Sueur	
		S. P. U. Pickering	
		W. M. Roberts	
		S. Smiles	
		Miss G. M. Walsh	
		A. W. Stewart	
		371	0 0
Commission on Recovery of Income Tax			
Balance, being Excess of Income over			
carried to Balance Sheet			
46	2 1	Expenditure	
7	10 1	...	
3	4 0	...	
18	10 6	...	
£401	5 0	...	
Repayment of Research Grants :—			
R. D. Abell			
J. W. Mellor			
E. A. Werner			
J. C. Cain			
F. G. Pope			
T. S. Price			
Miss I. Smedley			
A. J. Almond			
H. W. Bywaters			
W. B. Tuck			
Miss A. Homer			
N. L. Gebhard			
J. A. Carpenter			
1	16 2	...	
2	4 9	...	
6	9 6	...	
4	5 6	...	
7	1 4	...	
16	2 4	...	
5	10 4	...	
2	12 11	...	
7	0 0	...	
3	6 9	...	
17	16 3	...	
46	2 1	...	
7	10 1	...	
3	4 0	...	
18	10 6	...	
£401	5 0	...	
Sale of old platinum			
Return of Cost of broken apparatus			
Income Tax Recovered			
46	2 1	...	
7	10 1	...	
3	4 0	...	
18	10 6	...	
£401	5 0	...	

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

19th March, 1911.

Approved—
VICTOR H. VELEY.
FREDERICK B. POWER.
JOHN M. THOMSON.

this must be our usual condition. This undesirable result on the year's working has been brought about by several causes acting simultaneously.

The increase in income for 1909 over that for 1908 was £252, whilst that for 1910, from all sources, only exceeded that for 1909 by £59 17s. 10d., the respective amounts being £7,447 5s. 10d. for 1910, and £7,387 8s. for 1909. Whilst our income has improved so little, the expenditure has risen from £7,028 3s. 5d. to £7,594 12s. 2d., an increase of £566 8s. 9d. As mentioned earlier in the report, the volume of our *Transactions* has increased by more than 500 pages, that is, roughly, a quarter more than last year. This is reflected in the increase of £399 7s. 5d. in the cost of the Journal alone. Administrative expenses have also increased much more than usual, owing to certain expenses which had to be met this year of an abnormal character, and which are not likely to recur for several years. The total increase under this head is £188 4s. One other item which calls for remark is the large deficit on the Dinner Account, which has to be met from the funds of the Society. This time it amounts to £91 15s. 2d., but it ought to be pointed out that this is unusually high, and is due, in part, to the postponement of the Banquet from May 26th until November 11th, necessitated by the death of King Edward on May 8th. In view of the narrow margin between our income and expenditure it is to be hoped that some satisfactory method of avoiding this drain upon our resources may be devised and adopted in arranging for the next Anniversary Dinner, which, in the ordinary course, should fall in March, 1913.

Since the Officers of the Society have undertaken the management of the advertisements a profit of £75 12s. 5d. has resulted, whereas last year our net gain from this source was a little under £10.

The snapping of one of the links with the past, which all must regret, has been brought about by the death, in September, of Mrs. Emily Hall. The pension of £30 a year, granted in 1903 to Mrs. Hall on the death of her husband, Mr. Josiah Hall, for twenty-five years the courteous collector for the Society, thus lapses.

The income of the Research Fund exceeds the expenditure by £29 6s. 5d. This is due chiefly to the balances of grants made in previous years which remained unexpended having been returned by the grantees. These amount to £46 2s. 1d., and this sum is now available for redistribution. The normal income of the Fund is £344, and a sum of £371 was divided amongst forty-eight applicants in amounts ranging from £5 to £20.

A Vote of Thanks to the Treasurer, Hon. Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Mr. A. D. HALL, seconded by Mr. J. SPILLER, and acknowledged by Dr. J. J. DOBBIE.

The PRESIDENT then delivered his address, entitled, "On the Initiation and Propagation of Explosions." Sir WILLIAM TILDEN proposed a Vote of Thanks to the President, coupled with the request that he would allow his Address to be printed in the Transactions; the motion was seconded by Sir WILLIAM RAMSAY, and carried with acclamation, the PRESIDENT making acknowledgment.

The Scrutators then presented their Report, and the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year:

President: Percy F. Frankland, Ph.D., LL.D., F.R.S.

Vice-Presidents who have filled the Office of President: H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; H. B. Dixon, M.A., Ph.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; R. Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; the Rt. Hon. Sir Henry E. Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William A. Tilden, D.Sc., F.R.S.

Vice-Presidents: G. T. Beilby, LL.D., F.R.S.; J. Norman Collie, Ph.D., F.R.S.; M. O. Forster, D.Sc., Ph.D., F.R.S.; A. Liversidge, LL.D., F.R.S.; W. J. Pope, M.A., F.R.S.; J. Walker, D.Sc., Ph.D., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries: Arthur W. Crossley, D.Sc., Ph.D., F.R.S.; G. T. Morgan, D.Sc.

Foreign Secretary: Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council: W. A. Bone, D.Sc., Ph.D., F.R.S.; W. R. Bousfield, M.A., K.C.; Adrian J. Brown, M.Sc.; J. B. Cohen, Ph.D., B.Sc.; C. F. Cross, B.Sc.; C. E. Groves, F.R.S.; A. R. Ling; A. McKenzie, M.A., D.Sc., Ph.D.; Hugh Marshall, D.Sc., F.R.S.; J. C. Philip, M.A., D.Sc., Ph.D.; Sir Boverton Redwood, D.Sc.; A. E. H. Tutton, M.A., D.Sc., F.R.S.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 23rd, 1911.

By HAROLD B. DIXON, M.A., Ph.D., F.R.S.

The Initiation and Propagation of Explosions.

MODERN custom has decreed that the retiring President must address you, not on the affairs of the Society in which he has busied himself during his years of office, but on the chemical ideas those affairs have left him so little leisure to cultivate—lest, perchance, his ideas, if any, should fade into oblivion for want of an occasion like the present. I am not sure the modern custom is superior in all respects to the older practice, when the President reported on what the Council had done, and sometimes indicated what the Council might, or ought to, do; for if a President is reasonably attentive to his duties he must have attained in two years a fair working knowledge of the Society's business, and even have learnt something of the inner springs which move the wheels. Moreover, at the end of his term of office he is in the happy position of being quite disinterested in any advice he may give.

Now astronomers tell us that a comet, coming from the outer darkness into the blaze of perihelion, reveals to us by its partial dissipation facts about those forces of attraction and repulsion which control our system—facts we might never have learnt from the sun's less-eccentric attendants. In the same way, a President, coming from the provinces to this centre of light, might reveal (I don't say in moments of dissipation) something of the inwardness of our constitution, for—like the comet—before he vanishes once more into space he comes into very close relation with the controlling body, and is certain to experience, as chairman, the cosmic truth of the dictum that “heat is a mode of motion.”

Although, then, I see some advantages in the old ways, I bow, of course, to the new custom, and will ask you to listen once more to experiments and ideas on explosions; but before I do so I crave to make one confession of a personal kind, wrung from my experience as President. Looking, in the old days, at our central system from a distance, I may have thought, as perhaps other ordinary Fellows have thought, that those set in authority over us were occasionally autocratic in their views, and were wont to treat any departure from orthodox uniformity with the drastic methods we

associate with Procrustes. Accordingly, when this greatness was thrust upon me, it seemed natural to ask myself, with Malvolio, whether I could "be opposite with" the Publication Committee, whether I could "be surly with" the Editor? I have now watched that Committee at work for two years, and on retiring from the Chair, I think it only just to record my deliberate opinion that those who are responsible for our publications (whatever human frailties they may have) have shown, not only the pagan virtues of hard-work and devotion to the interests of the Society, but have proved they possess also the more Christian virtues of kindness and long-suffering. *Credite posteri!*

• *The Pre-flame Period of Combustion.*

In my address last year I pointed out that the existence of the pre-flame period of combustion prevented the method of adiabatic compression being used for determining the ignition-points of *slow-firing* mixtures of gases unless the piston were artificially arrested at the moment the ignition-volume was reached. A further study of the effects produced by the sudden compression of gaseous mixtures has revealed, not only *the actual forward movement of the piston* while the flame is spreading, but also the importance of the "pre-flame" period of combustion.

Without going into details, which I hope the Society will publish in a separate paper, I might refer here to some of the chief results obtained when an explosive mixture of gases is rapidly compressed in a long cylinder by a piston:

(i) If the piston is stopped artificially before the "ignition-point" is reached, a very slight combination is found to have occurred. By repeating the compressions with the same mixture ten or a dozen times, and bringing the gases to within 2 or 3 degrees of their ignition-point each time, it is possible to show that combination has taken place; for example, in mixtures of carbon monoxide and oxygen about 1 per cent. of carbon dioxide has been measured.

(ii) When the ignition-point is reached, the gases unite sufficiently rapidly to self-heat the mixture (after the motion of the piston is stopped), the evolution of heat by the chemical reaction being greater than the loss of heat to the cold walls of the vessel.

(iii) The gases, self-heated by this pre-flame combination to a temperature much above the "ignition-point," burst into flame at some spot, from which the flame spreads throughout the column with a velocity depending on the nature of the mixture, and on the extent of the compression.

(iv) If the piston is not checked when the "ignition-point" is reached, it continues to move forward until stopped by the explosion, *i.e.*, it moves forward during the pre-flame period (which it shortens by raising the temperature), and during the lesser period occupied by the spread of the flame. If, therefore, the "ignition-point" is calculated from the position reached by the piston when stopped by the explosion, that temperature will be too high, except in those cases where the length of the pre-flame period and the time taken for the flame to spread are negligible.

As illustrating the great importance of the pre-flame period of combustion, I might refer to four photographs of the flames produced when successive portions of the same gaseous mixture were compressed under the same conditions, except that the piston was allowed to travel further (before being artificially stopped) at each repetition of the experiment.

The camera being fixed with the film moving vertically downwards, the glass explosion-tube (13 mm. in diameter) was held horizontally, and the piston was driven in by a heavy pendulum (3 metres in length) allowed to fall from a known height. The pendulum itself was stopped by a firmly-fixed steel barrel, through which the piston, together with several outer tubes encasing it, slid smoothly. These tubes, sliding one inside the other, as in a telescope, prevented the long piston from buckling under the sudden thrust.

A slow-firing mixture containing one volume of hydrogen and three volumes of oxygen was employed. When a column of these gases 540 mm. long was compressed into a length of 40 mm., no flame was produced; but when the same column was compressed into a length of 36 mm. before the piston was stopped, a flame appeared in the centre of the compressed gases, as shown in Fig. 1. On the assumption that the ratio of the specific heats of the compressed gases is 1.4, and that there was no loss of heat during compression, the gases were heated by the compression to a temperature of 550° in the first, and of 578° in the second experiment. On these assumptions the "ignition-point" of this mixture would lie between these two temperatures.

In the next experiment the piston was not stopped until the column of gases was compressed from 540 mm. to 30 mm. The temperature of the gases, calculated from the compression alone, must have been at least 640° at the moment the flame first appeared, for the photograph (Fig. 2) shows that the piston could not have moved more than 0.5 mm. during the spread of the flame, and, consequently, the gases must have been compressed to 30.5 mm. at least before the flame started.

In the fourth experiment the piston was not stopped until the column of gases was compressed from 540 mm. to 20 mm., and the flame (Fig. 3) did not appear until the piston reached this point, or was not more than 0.5 mm. from it. The temperature of the gas, *calculated from the compression alone*, must have been at least 810° at this moment. In the fifth experiment the piston was not stopped until the column was compressed to a length of 13.5 mm. If the flame started when the piston was 0.5 mm. from its stopping place, and the photograph (Fig. 4) shows that it could not have started before, the temperature of the gas, *calculated from the compression alone*, must have been at least 975° before the flame appeared.

It is evident, then, that the "ignition-point" of this mixture (according to the first experiment, below 578°) is a long way below the temperature at which the flame actually appears.

Some idea also may be formed from these experiments as to the time which elapsed between the moment when the "ignition-point" was reached and the moment when the flame started. If we assume that the ignition-point was just reached in the second experiment when the temperature was about 578° , and the piston was 36 mm. from the closed end of the tube, we may also assume that the ignition-point was reached in the fifth experiment when the piston arrived at the same place in its forward movement. But the photograph shows that in the fifth experiment the piston had time to travel forward at least 22 mm. from this position before the flame appeared. The time required for the piston to travel this distance was at least 7 mille-seconds. The heat produced by the compression from 36 to 14 mm. would have raised the temperature of the gases from 578° to 975° (approximately), and this rise of temperature would have hastened the self-heating. A pre-flame period of 7 mille-seconds is therefore a *minimum* for this mixture when brought to the "ignition-point." On the other hand, by making the pendulum break an electric circuit just when the piston was stopped 36 mm. from the end of the tube, it was possible to photograph a spark on the moving film, and so to measure the time-interval between the spark and the first appearance of the flame. This gives the pre-flame period about 13 mille-seconds when the retardation of the spark is taken into account. The pre-flame period is therefore of the order of 10 mille-seconds (or 1/100th of a second) for this mixture under the conditions of the experiment.

As another illustration of the extent of the pre-flame period, I might refer to the experiments now being carried on in my laboratory by Messrs. Ramsbottom and Crofts on the adiabatic compression of carbon monoxide and oxygen. When the mixture is dried by

passing through sulphuric acid and the piston is stopped artificially, they obtain a fairly constant ignition-point of 485° , and when the mixture is dried by passing through a long column of phosphoric oxide, the ignition-point is 504° ; whereas when the piston was allowed to travel until stopped by the explosion itself, K. G. Falk found an ignition-point of 601° .

Messrs. Ramsbottom and Crofts have also repeated my experiments with different mixtures of hydrogen and oxygen, and confirm the preliminary results I announced last year, viz., that the ignition-point falls regularly when oxygen is added to electrolytic gas. The chief difference found with a rather larger cylinder and with further precautions to prevent leakage, is that the ignition-points of the several mixtures come out lower.

The self-heating period of flameless combination between the "ignition-point" and the appearance of the flame is seen from these experiments to be an important phase of gaseous combustion. The phase may be controlled and, as it were, steadied by contact with hot surfaces, which prevent the development of a flame temperature. It is to this period or phase of slow chemical combination that most of the experiments that have been made on the influence of water-vapour apply. In the case of electrolytic gas, my experiments confirm those of Dr. Brereton Baker that the presence of some water molecules facilitates the flameless combustion. If, at this temperature, water molecules could remove a negative electron from hydrogen, or convey one to oxygen, or transfer one from hydrogen to oxygen, the water might induce chemical change, acting, as Professor Bone in his very suggestive experiments has shown, as gold and silver surfaces act towards hydrogen and oxygen when heated in these gases. It would seem as if the flame marked the abrupt beginning of another mode of chemical combination, a mode independent of water molecules.

The Initiation and Spread of the Flame.

When the mixture of gases is brought to the "ignition-point" by sudden compression, and the piston is arrested, the flame appears (after an interval) at some point in the gaseous column, and spreads more or less rapidly, according to the nature of the mixture and to the compression employed.

To study the initiation of the flame, Dr. L. Bradshaw and I have largely employed a mixture of carbon disulphide with oxygen on account of its low ignition-point and of the actinic character of its flame. Narrow, vertical strips of black paper were fastened on the tube at intervals of 25 mm. from the closed end; these, focussed on the film, form vertical dark lines on the prints at intervals of 6 mm.,

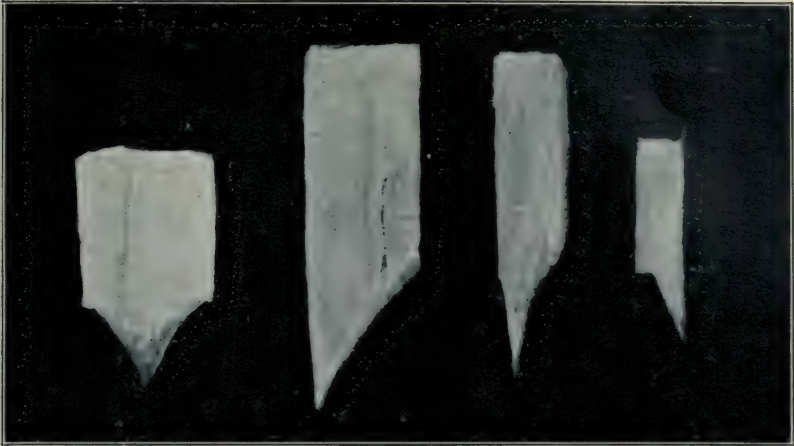


FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

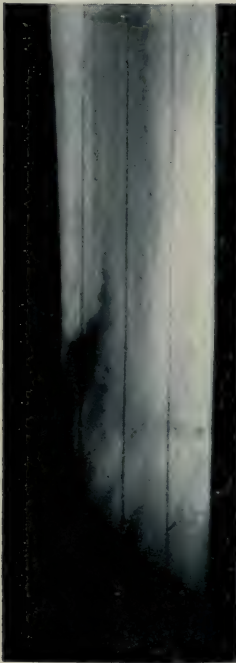


FIG. 5.



FIG. 6.



FIG. 7.



FIG. 8.



FIG. 9.



FIG. 10.

FIG. 11.

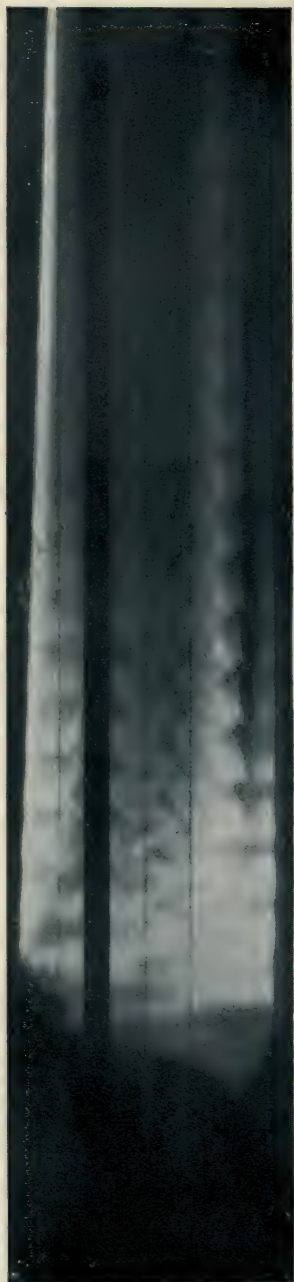


FIG. 12.

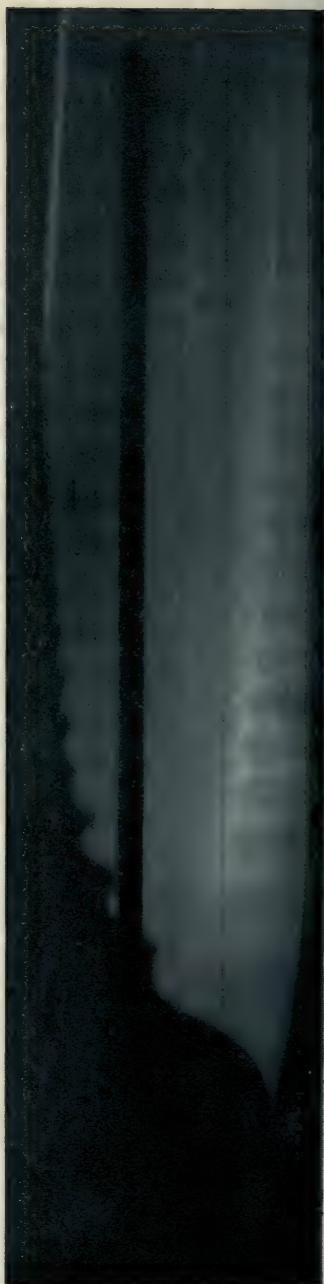


FIG. 13.

and serve as reference marks. The horizontal movement of the flame along the tube is thus reduced in the photograph to about one-fourth of its true amount, while the vertical movement is that of the film.

Figures 5, 6, and 7 show the flames produced in the mixture $2\text{CS}_2 + 5\text{O}_2$ when a column of the mixed gases 630 mm. long was compressed successively to 86 mm., 67 mm., and 60 mm. respectively. In each case the piston was driven in from the left side, and the film was moving vertically downwards at a rate of 20 metres per sec. The maximum compression is shown by the position of a small collar sliding on the piston. The piston stopped the moment the moving force of the pendulum was removed.

In Fig. 5 the flame is seen to start near the closed end of the tube, and to travel towards the left with an increasing velocity, which reaches about 100 m. per sec. The flame is then checked (near the second reference mark) by a sound wave, and afterwards it travels unevenly and more and more slowly until it reaches the piston, which is slowly pushed out by the hot gases.

In Fig. 6 the flame started some 16 mm. away from the closed end from a less well-defined point.

In Fig. 7 the flame appeared almost in the centre of the column of gases, and its starting point is still less defined.

Fig. 8 and Fig. 9 show the flames produced in two experiments where all the conditions were the same, except that the pendulum was moving more slowly in the second case. In Fig. 9 the flame spread from the firing-point with a velocity not greater than 14 m. per sec. It is to be remembered that in this mixture the velocity of the explosion-wave is nearly 1800 metres per second.

With mixtures of carbon disulphide the spreading flame was sometimes bright enough to show a reflexion from the polished end of the steel piston. When the moving pendulum was artificially stopped, as in the above figures, this reflexion can be seen on some of the films as a *vertical* line, showing that the piston had stopped when the flame started; but when the pendulum was allowed to swing until its motion was stopped by the flame itself, the line of light produced by the reflexion from the piston is seen to be *inclined*, showing that the piston was moving inwards while the flame was travelling outwards to meet it.

With mixtures of hydrogen and oxygen the photographs show that the explosion-wave is only set up in the mixture $\text{H}_2 + 3\text{O}_2$ when great compression is employed (Fig. 4), and after the initial flame has nearly traversed the column of gases. On the other hand, with electrolytic gas, though the flame always appears to start at some point, the explosion-wave is very rapidly set up. It was very

difficult to find glass tubes that would stand the firing of electrolytic gas by adiabatic compression. But the glass usually did not break until the flame had spread through the tube, and lasted long enough to afford a sharp photograph of the whole column of ignited gas. With the film moving 50 metres per second, it is possible to trace the spread of the flame from the firing-point in electrolytic gas, though in some cases most of its path appears to be traversed instantaneously; for example, in Figs. 10 and 11 the explosion-wave was set up before the flame had travelled far from the firing-point. Even when great compression was used, the gases fired at a point from which the flame spread.

In the experiments so far made, little evidence has been detected of any violent compression-waves set up by the movement of the piston. Of all the photographs taken of different gases fired by compression, Fig. 5 is the only one that shows clear evidence of waves interfering with the flame, and these waves appear to be the result of the initial flame itself rather than of the movement of the piston. The waves shown in Fig. 5 are in marked contrast to those obtained in former experiments when the gases were fired by a spark under normal pressure. In order to study what effect strong compression-waves would have on the flame under high pressure, the apparatus was arranged so that the pendulum might break the primary circuit of a coil during its fall, and so induce a spark between platinum wires inserted near the closed end of the tube. The gas could thus be fired either by compression alone or by means of a spark at any time during the compression.

Fig. 12 shows the flame produced in the mixture $\text{H}_2 + 3\text{O}_2$ when it was sparked during compression. The spark was passed (20 mm. from the closed end) when the column had been compressed from 560 mm. to 150 mm., and was consequently at a temperature of about 220° . The sound-waves starting from the spark are strongly marked. In Fig. 13 a similar column of the mixture $2\text{CS}_2 + 5\text{O}_2$ was compressed to 170 mm. before the spark was passed. Both flames show the characteristic reflexions produced by sound-waves starting from a "sparking" place.

It is clear from these photographs that no marked sound-waves are produced by the movement of the piston in the act of compression. It is also clear that the flame set up by the compression of the piston does not give rise to the well-defined waves which are so conspicuous in the spark-ignited mixtures. The "compression-flame" has not the same sharp beginning; except when it starts close to one end of the tube, it seems to emanate from a wider area, and its advancing edges are less clearly defined than the "spark-flame."

This confirms an observation which Dr. Coward and I made on the ignition of an axial jet of hydrogen mixing with an outer stream of oxygen in a heated tube. We noticed that the flame began in a large sphere of pale light, which contracted abruptly into the small central flame.

These experiments bring out one fact of great importance in the theory of the explosion-wave. It has been usual to assume, following Le Chatelier, that if a layer of gas is brought to its ignition-point by adiabatic compression, *e.g.*, if, in a column of mixed hydrogen and oxygen, a layer is suddenly compressed by any means to $1/14$ th of its initial volume, then that layer will be fired, and by its expansion will compress the next layer to its firing-point, and the flame will be propagated from layer to layer as an "explosion-wave." But the photographs show that the mere heating of a mixture of explosive gases to the ignition-point by adiabatic compression does not necessarily set up the explosion-wave; and even after the flame is started it may spread comparatively slowly through the already heated and compressed mixture. To start the flame at all, the gas must be far above the "ignition-point": to propagate the explosion-wave, evidently something more is required than that each layer should be compressed to the ignition-point and be in contact with a burning layer. It seems to me that the flame can only advance as an explosion-wave when, not only a few, but the great majority of the molecules in the wave-front have sufficient translational energy to combine chemically on collision.

Former experiments have shown the extraordinary abruptness with which the full intensity of the explosion-wave is set up. When the explosion-wave is analysed with a film moving 100 metres a second, there is no indication of any preliminary brightening up of the flame. If the burning of each molecule depended on a number of successive molecular collisions, such as no doubt occur in the thickness of the column making up the visible flame, I do not see why the flame should begin so sharply, on the contrary, I should expect the front of the advancing wave to be preceded by a *corona*; nor do I see why the flame should advance with the velocity of a *sound-wave* in the burning gases.

It is otherwise with the *secondary* reactions taking place in the flame. These prolong the flame, as I have shown in the burning of cyanogen to carbon dioxide; and I should like to recall attention, in this connexion, to some experiments I made many years ago on the influence of a cold surface on the equilibrium reached in a flame when one of the reacting gases was condensable.

When a mixture of hydrogen and carbon monoxide is fired with insufficient oxygen for complete combustion, the primary reaction

is followed by a reversible change between the unburnt and burnt gases:



Of these reacting gases the steam is condensable at the ordinary temperature. The great change in the equilibrium produced by condensing the steam *while the reaction is proceeding* is shown in the following table. Below the condensing point of the steam, changes of temperature of the walls greatly influence the equilibrium; above the condensing point of the steam, changes of temperature of the walls make no difference.

Temperature of containing vessel.	Equilibrium found
	$= \frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2}.$
- 10°	7·0
0°	5·9
20°	5·2
40°	4·5
60°	4·1
80°	4·0
100°	4·0
125°	4·0

Coal-dust Explosions in Mines.

In face of the terrible coal-mine explosions of last year—that at Whitehaven, and that more recently at Hulton—it cannot be said that the mechanism of the initiation and spread of the explosion-flame is of merely theoretical interest. The presence of finely divided coal-dust in the workings and roadways of a mine has long been known to add to the danger of fire-damp explosions, but it is only in recent years that it has been recognised that fine coal-dust suspended in the air forms an explosive mixture through which flame is propagated with the rapidity and violence characteristic of true explosions. This truth has only been slowly established by the careful observation of the conditions of many devastating explosions in mines, and by the work of many experimenters at home and abroad, among whom I should like to name Mr. William Galloway as a pioneer. Even when it was demonstrated that coal-dust *per se* could propagate an explosion—as in the Camerton explosion in 1893, and in the experiments of Sir Henry Hall at Ormskirk—it was still imagined that the conditions for a dust explosion must be exceptional, and in France the danger was almost disregarded until the terrible proof afforded by the disaster at Courrières. Nearly twenty years ago, as a member of the Royal Commission on the explosion of coal-dust in mines, I supported Mr. W. E. Garforth's plea for making a full-sized experimental gallery, and urged the necessity of making trials on a working scale

to determine the nature of the waves set up in a dust explosion. It was useless, for instance, to advocate "dustless zones" as a remedy until one knew the power of the flame to leap such dust-free spaces. I was met by the arguments:—(i) such experiments would be very expensive; (ii) if they were made outside a mine, they would not carry conviction to mining men; and (iii) since a dust explosion can only be started by a blown-out shot or by an ignition of fire-damp, it is better to concentrate attention on flameless explosives, and seek means to prevent the initial flame. Unfortunately, as I think, these arguments prevailed.

At the present day, the opinion of practical and of scientific men who have studied the question, is in favour of full-scale experiments. In France and in England experiments have been made during the last two years on a scale which, at least, affords conclusive evidence of the initiation of true explosions of coal-dust and air. At Liévin and at Altofts experiments have been made which demonstrate beyond all question the extreme explosiveness of finely divided coal-dust, and most valuable information has been gained as to the power of the flame to penetrate through a dustless zone to dust-laden air beyond, and as to the damping effect of stone-dust on the ignition of coal-dust by a blown-out shot. The country owes much to the public spirit of the Mining Association of Great Britain, at whose cost the experiments at Altofts have been made, under the personal superintendence of Mr. W. E. Garforth.

An iron gallery, 600 feet long and $7\frac{1}{2}$ feet in diameter, was constructed of cylindrical boilers bolted together. Inside a tram-line on a concrete floor, with props and cross-timbers placed at 9 feet intervals, made a travelling road, comparable with the main haulage-road of a mine. Shelves fastened to the sides provided ledges for holding dust, and the flame of a blown-out shot was reproduced by firing a stemmed gun-powder charge from a cannon. Just before firing, a current of air was drawn into the main gallery by a fan placed at the end of a "return" gallery. By this means a pure coal-dust explosion, extending over several hundreds of feet, could be obtained, and the propagation of the flame and pressure studied.

But in addition to the main demonstrations carried out in this gallery, a laboratory was fitted up for experimental work on the heating of coal, and the Chemical Society has already had important papers describing the work done there by Dr. R. V. Wheeler, who was placed in charge of the scientific experiments.

So far as the tests have extended, the propagation of the coal-dust flame appears to be similar to that of the flame in mixtures of coal-gas and air, or of fire-damp and air. After the flame has

travelled some distance, without great velocity or violence, vibrations are set up which may attain considerable amplitude, and give rise to local areas of great pressure. The vibrating flames advance with *average* velocities of 300 to 400 feet per second, the average velocity increasing with the length of run. No steady maximum velocity—the characteristic of the “explosion-wave”—has been observed, although pressures between eleven and twelve atmospheres have been registered. One curious parallelism between the initiation of a dust and of a gas explosion has been noticed. When the dust is ignited in the middle of the empty gallery without obstructions such as the props afford, the explosion is slow and feeble. The burning of a gaseous mixture in a small tube is similarly slow and non-luminous at first, unless the flame reaches one end of the tube, or an obstruction, from which a wave can be reflected back.

Again, and this is an important point, Dr. Wheeler has shown that the coal-dust raised and suspended in the air does not undergo a preliminary distillation by which a mixture of gas and air is made, but that it ignites as a solid *whole*. Of course, in the flame (behind the wave-front) the coal undergoes a distillation process, but that is a secondary change, and is not the cause of the ignition which propagates the flame. Dr. Wheeler has shown in the experimental gallery that an explosion is propagated through a cloud of charcoal-dust in air.

While the experiments made at Altofts have given most valuable information, it is evident that the work should be completed on the lines so successfully begun. In particular, it is essential to discover how far the explosive violence of the flame may extend, what limit short of the explosion-wave is reached—not only with dust alone, but when small quantities of fire-damp help to start the flame. But the limit of such experiments in the immediate vicinity of a colliery and a mining village has been already reached. The Mining Association has offered all the plant and instruments to the Government if they will complete the investigation. Here is the opportunity for a truly national work, which cannot be said to be premature or uncalled for: I do not think a Government which has at heart the interests of industry and labour, can let it pass.

And now, in taking my leave of you and yielding the Presidential chair to my distinguished friend, who, we are all proud to remember, greatly wears a name great in chemistry, I desire to express to my colleagues on the Council, and especially to the senior Secretary, my warmest thanks for their kindness and consideration; and to

the Fellows I would say: "I am truly grateful for your uniform courtesy and forbearance; I have learnt, I trust, something from your papers and discussions, and this, at least, I have learnt—that there is brilliant talent and most earnest devotion to science in your midst. That you have thought me worthy to be your President, I shall treasure as the great honour of my life."

OBITUARY NOTICES.

RICHARD ABEGG.

BORN JANUARY 9TH, 1869; DIED APRIL 3RD, 1910.

RICHARD ABEGG, who joined our Society in 1906, was one of those lovable characters whose pleasure it is to help others, without thought of self. All who knew him personally deplored the terrible accident which cut short his career in the full vigour of his strength, for it deprived them of a true and valued friend; and the loss to science of one who had so successfully devoted his life to its furtherance, both by example and as a teacher, was acknowledged by all those to whom his work was known.

Abegg was the son of Wilhelm Abegg, Legal Advisor to the Admiralty, and Margaret (*née* Friedenthal), both of whom survive him. His grandfather, I. F. Heinrich Abegg, was the well-known Professor of Criminal Law in Breslau; the family was of Swiss origin. He was born on January 9th, 1869 at Danzig, but received his school training in Berlin, where his parents settled when he was a child. Even as a schoolboy, he had a small private laboratory, to the annoyance of his mother, to whom chemical smells were not grateful. His student days, from 1886 to 1890, were spent with Lothar Meyer at Tübingen, with Ladenburg at Kiel, and with Hofmann at Berlin. There he graduated in 1891, his dissertation treating of "Chrysene and its Derivatives." In that year he became a pupil of Ostwald at Leipzig, and in 1892–3 of Arrhenius in Stockholm. During his student days he fulfilled his military duties; in 1891 he was an officer in the Reserve, and in 1900 Oberleutnant in the Reserve in the 9th Regiment of Hussars. It was in that year that he made his first balloon ascent, for military purposes, and he was so charmed with the experience that he and his wife shortly after made another, and from time to time they indulged themselves in that pastime, with what a fatal result we

all know and regret. During his voyages in the air he made many scientific observations, which are still unpublished.

In 1894, Abegg became "Privatdozent" and assistant to Nernst, then Professor of Physical Chemistry in Göttingen; while there he was granted the title of professor, on the occasion of the opening of the new buildings. A year later, he was happily married to Line Simon, daughter of Commerzienrat Simon; and in 1899 he was elected "Abteilungsvorstand" of the Chemical Laboratories in Breslau. He received a call to Christiania in 1901, as successor to the celebrated Waage, but declined it; and in the same year he was granted the title of Extraordinary Professor at Breslau. A year before his death he had been appointed full professor in the Technical High School at Breslau, and had erected new chemical laboratories there, which, alas, he was not destined to conduct. While Abegg was teaching at Breslau, many of our countrymen were among his students; Steele, now Professor at Brisbane; Fox, now at Poona; Denison, now in Natal; Hadfield, now with Zeiss at Jena; Cumming, Knox, Gibson, Jackson, Johnson, and many others, when working in his laboratory, learned not only to respect him as a teacher, but to regard him as an intimate friend. For Abegg thought it his duty, as it certainly was his pleasure, to become intimate with his students; they were often in his house, and at Christmas time they joined in the family's festivities. At that time of year used to appear the "*Zeitschrift für Metachemie*," in which all sorts of absurdities were given forth in an apparently scientific paper, resembling in its get-up the "*Zeitschrift für Elektrochemie*," of which Abegg was editor from 1901 until his death. His was a rare character; unselfish and considerate of others; sanguine, in his hopefulness; untiring in his work; and full of new and useful ideas, with great conscientiousness, and devoted to his science and to his pupils.

No sketch of Abegg would be complete without allusion to his love of travel and sport. He was well set-up, active, and as untiring in his amusements as in his work; an excellent skater and "ski-er," fond of long tours on foot, and an ardent traveller. In 1896-7 he obtained six months' leave of absence, which he employed in a voyage to India, Ceylon, and Java; his experiences were published in a small volume entitled "*Indische Reise*."

Although Abegg was granted his degree by Hofmann on an organic thesis, he soon abandoned that branch of our science for the physical side, and was an ardent supporter of the views put forth by Arrhenius, van't Hoff, and Ostwald. He strove to promulgate these views by publishing, along with Herz, his "*Chemisches Praktikum*" for qualitative analysis (1900), in which the ionic

nature of the fundamental reactions was insisted on. Another useful work from his pen was his "Anleitung zur Berechnung volumetrischen Analysen" (Breslau, 1900); and in 1903 he wrote on "Die Theorie der elektrolytischen Dissoziation," an English translation of which was published by Wiley, of New York, in 1907. With Dr. Sackur, too, he published, in 1907, "Physikalisch-chemischen Rechenaufgaben," a series of examples of calculations in physical chemistry, which met with much acceptance.

But Abegg's name will live in connexion with his great undertaking, the "Handbuch der anorganischen Chemie" (Hirzel, Leipzig, 1905-9). In his preface, Abegg drew attention to the fact that before the inception of this work, "the rich harvest of physico-chemical investigations, partly owing to their appearing in special journals, partly owing to the difficulty of presentment, had often not been accorded that place in chemical literature which their importance merited." He intimated that the scope of this monumental work would be "to present these additions to knowledge in an easily understood form, and to show their close relationship with the other results of investigations in inorganic chemistry," and went on to say that "where possible, special attention would be paid to the theoretical bearing of chemical facts, which up to the present have merely been recorded." His intention was to elevate chemistry from its old position as a descriptive science into a rational one. It is generally acknowledged that in the four parts of this work which have been published, he and his collaborators have done much to fulfil the aspirations of the editor.

One of Abegg's early and important contributions to chemical knowledge was his "Studies on the Freezing Points of Concentrated Solutions," in which he showed that the deviations exhibited by such solutions correspond with the deviations from Boyle's law due to the increase of the number of molecules per unit volume. This research, carried out in 1894, was succeeded by another, in which he studied very dilute solutions of non-electrolytes, and showed that they show the relations stated by Blagden and by van't Hoff, and also that the amount of ionisation of electrolytes, measured by cryoscopy, agrees within narrow limits with that deduced from electric conductivity. Later, in 1897, he worked at dielectric constants, and determined the variation of these magnitudes with temperature. Other subjects of research, partly by himself, partly with pupils, related to the solubility of ammonia in salt solutions, the direct determination of the mobility of ions, the solubility of sparingly soluble salts, and the vapour pressures of ammonium chloride.

From 1899 on, Abegg published on "Valency and the Periodic

System." According to his theory, the elements possess amphoteric properties, *i.e.*, the power to form compounds both with positive as well as with negative ions. The valency of an element is a variable quantity, so that both its positive and negative valency exhibits a maximum; the sum of both these maxima is 8. The smaller number of both maxima corresponds with the stronger valencies, which he named the "chief valency"; the others were termed "contravalencies." This theory, as pointed out by him, is somewhat similar to the abandoned view of Berzelius, and has a certain relationship to the doctrines expounded by Helmholtz in his Faraday Lecture. But the regularity of the behaviour of elements is not general, but is apparently connected with the irregularities of the periodic system. In his "Handbook," these views are developed, and it is certain that he would have contributed other important additions to our knowledge of valency.

Had Abegg lived, there can be no doubt that he would have become one of the leaders of German science, not merely by his ability, his power of influencing others, and his unusual energy, but also by his personal character, which was one that commanded respect and affection from all who knew him, and would have placed him in the front rank of scientific men, without respect to country.

W. R.

MICHAEL CARTEIGHE.

BORN 1841; DIED MAY 30TH, 1910.

MICHAEL CARTEIGHE, whose death occurred at Goring-on-Thames on May 30th, 1910, was born in Lancashire, of Irish extraction, in 1841. He was elected a Fellow of the Society in 1864, and was a Member of Council from 1878 to 1882, and also from 1884 to 1888. Such is the brief record of his official connexion with the Society, but those only who have been his fellow-workers, or who knew him personally, can well appreciate the loss sustained by the death of one who was a man of exceptional intuition and business capacity, of wide knowledge of the world, of enthusiasm for the advancement of physical and chemical science, and one who was ever ready to encourage the student by wise counsel or by material help. Although he contributed no papers to the Proceedings and Transactions, the interests of the Society always received from him the most enthusiastic and liberal support. He gave early indications of an interest in, and a capacity for, chemical and physical research

as a student at University College, where, later, as a demonstrator under Williamson, he took part, with Matthiessen and Holzmänn, in some researches in the electrical conductivity of alloys; the results of this work were embodied in a communication to the Royal Society. Just at this critical moment of his career, however, circumstances shunted him to the side-track of pharmacy, and thenceforth his chief, though by no means his only, interests were to be centred in the educational, political, and general progress of the Pharmaceutical Society of Great Britain.

On leaving University College, he entered the School of Pharmacy in Bloomsbury Square, in which he was a distinguished student, carrying off in 1862 its highest award, the Pereira Medal. He was for many years an Examiner of the Pharmaceutical Society and a Member of Council, whilst for fourteen consecutive years (1882-1896) he was President of the Society. In these important positions he always kept before his fellow-workers a high ideal of educational progress, and he was never tired of insisting on the value of a sound scientific training as a foundation on which to build useful and remunerative work in after life. In support of these views, he was largely instrumental in the institution and development of a Research Department of the School of Pharmacy, from which has emanated much valuable work. Michael Carteighe was one of the founders of the Institute of Chemistry, and a member of the first and succeeding Councils for a total period of fifteen years; he was also Vice-President for six years, and Censor for three years. His name appears in the list of petitioners for a Royal Charter, and it is well known that he used his great influence and gave much time and energy in support of the petition, which was granted in 1885. He was Honorary Secretary of the British Pharmaceutical Congress from 1880 to 1882, Honorary Secretary of the International Congress of Pharmacy in 1881, six years Vice-President of the Royal Society of Arts, a member (1893) of the Royal Commission in connexion with the Chicago Industrial Exhibition, Fellow of University College, Member of the Royal Institution, and Honorary Member of many foreign Pharmaceutical Associations.

It is impossible in this slight sketch of his career to give the reader an adequate idea of the unique personality of Michael Carteighe, a man of unfailing *bonhomie*, of untiring energy, of undoubted capacity, and yet withal of tender sympathy, and finally of an inexpressible cheerfulness which could face, with patience and courage, first the partial, and then the total, blindness of the last two years of his active life.

WALTER HILLS.

OSCAR GUTTMANN.

BORN FEBRUARY 25TH, 1855; DIED AUGUST 2ND, 1910.

THE tragic death of Oscar Guttman, as the result of a motor-cab accident in Brussels, came as a terrible shock to those who had seen him full of life and activity a few hours previously, and was a grievous blow to his family and friends, as well as a great loss to the industry of explosives. He had just begun his duties as British Juror at the Brussels Exhibition when the fatal accident occurred which cut him off in his prime and at the height of a successful career.

Guttman was born at Nagy-Becskerek in Hungary. He began his technical career in a Cerasin factory, and at the age of twenty he entered the dynamite works at St. Lambrecht, in Austria, and thus commenced his connexion with the explosive industry which remained the main field of his work. He was successively employed in a guncotton factory near Ofen-Pest, in the Nobel dynamite factory at Iselten, in Switzerland, where the explosive for the St. Gothard tunnel was made, and as manager of the Nobel dynamite works at Avigliana, in Italy.

The literary ability which was a dominant feature of all his activity early showed itself, as he became the editor of *Der Bergmann*, an Austrian mining journal, at the age of twenty-three.

Guttman's connexion with this country began in 1883, when he visited it and had the opportunity of seeing many of the explosive factories. He communicated an account of this journey and his impressions to *Dingler's Polytechnisches Journal*.

In 1888 he started in Vienna as a consulting chemical engineer, and one of his first commissions was the erection of the works for the National Explosives Co. at Hayle, in Cornwall. This induced him, in the same year, to take up his residence in England, and he settled in London as a consulting engineer and chemical adviser, and soon took a leading position in matters relating to explosives in this country. He was a great linguist, and kept up his connexion with the Continent, where he had clients in many countries.

He also devoted attention to the improvement of the manufacture of nitric acid, and took patents for his well-known plant, which has been widely used, also for a process for the concentration of sulphuric acid, and for his "Reaction Tower." The last patent he took out was for the construction of safer buildings in explosive factories, on which he read a paper before the Society of Chemical Industry. The use of this patent he offered free to any who chose to adopt his proposals.

Guttman was a regular contributor to "Dingler" until 1891, and also wrote many papers for the *Zeitschrift für angewandte Chemie*, *Zeitschrift für das gesamte Schiess-und Sprengstoffwesen*, the *Journal of the Society of Chemical Industry*, and the *Proceedings of the Institution of Civil Engineers*. He was the author of "Blasting," 1892, and "The Manufacture of Explosives," 1895, which was his largest work and the best on the subject for many years. He delivered a set of Cantor Lectures at the Royal Society of Arts in 1908, which were afterwards published in book form under the title, "Manufacture of Explosives: Twenty Years' Progress." He also contributed the articles on explosives in *Chemische technische Untersuchungsmethoden* and *Muspratt's Encyclopädisches Handbuch der technischen Chemie*, besides suggesting and taking a most active part in the preparation of "The Rise and Progress of the British Explosives Industry," published by the Explosive Section of the Seventh International Congress of Applied Chemistry.

In addition to his writings on present-day explosives and allied matters, Guttman took a keen and loving interest in the historical and antiquarian side of his subject, and spent much time and money in collecting all the books and information he could. He gave out the result of his researches in the form of an édition de luxe entitled "Monumenta Pulveris Pyrii," which was issued to a limited number of subscribers.

He was a member of the Society of Chemical Industry, serving twice on its Council, and took an active interest in its meetings and work. He was also a vice-president of the Institute of Chemistry, and greatly assisted in the introduction of special technical examinations in connexion with that Institute, and he was a member of the Institution of Civil Engineers.

Guttman had probably one of the most complete collections of books and pamphlets on explosives. He had a remarkably accurate and comprehensive memory, and he had a wonderful faculty for collecting and indexing information about explosive subjects, which was of great advantage to his clients. He was a man of strong opinions and rather enjoyed controversy, but he was always ready and willing to acknowledge when he had been mistaken.

He had an amiable character, which was better appreciated as one became more intimate with him. He did many kind and helpful actions, and was particularly responsive to any kindness shown to himself. He leaves a widow, two sons, and a daughter, and his memory received a tribute any father might be proud to have inspired from a grown-up son, "He was the best man I ever knew."

W. M.

CHARLES HANSON GREVILLE WILLIAMS.

BORN SEPTEMBER 22ND, 1829; DIED JUNE 15TH, 1910.

CHARLES HANSON GREVILLE WILLIAMS, son of S. Hanson Williams, a solicitor, was born at Cheltenham, September 22nd, 1829. His death took place in his little cottage at Smallfields, Horley, on June 15th, 1910.

His early attempts to study practical chemistry did not receive the paternal approbation; indeed, on one occasion, when the boy's pocket-money, saved up for many weeks, had been expended in the purchase of a "chemical chest," the father, with a sweep of his cane, consigned the newly-acquired treasures to destruction.

It was at the house of Dr. J. H. Gladstone, in Tavistock Square, that the writer of this notice first met Greville Williams: this was in the early 'fifties—probably in 1852 or 1853—when the young man was at work as a consulting and analytical chemist in Oxford Court, Cannon Street. He soon migrated to Glasgow, on being appointed first assistant to Professor Thos. Anderson, of Glasgow University, for whom, during three years, he carried out much research work; afterwards he conducted a tutorial class under Dr. Lyon (since Lord) Playfair at Edinburgh. During 1857 and 1858 he was lecturer on chemistry in the Normal College, Swansea. In 1858 he returned to Glasgow as chemist to the works of George Miller and Co., manufacturing chemists. Greville Williams moved to Greenford Green in 1863, remaining with Messrs. Perkin until 1868, when he entered into partnership with M. Edouard Thomas and Mr. John Dower, at the Star Chemical Works, Brentford, the firm being makers of coal-tar colours and subsisting until 1877. Mr. (now Professor) R. Meldola, F.R.S., and, after his retirement in 1872, Dr. Otto N. Witt, were in the service of this firm as chemists. It was under the auspices of Dr. Witt that some of the first azo-compounds were manufactured in this country by the firm of Williams, Thomas, and Dower. On the closing of the works, Greville Williams gave up his connexion with manufacturing chemistry and became photometric supervisor to the Gas Light and Coke Company, with whom he remained until 1901. He then retired into the country, living the life almost of a recluse, and seldom seeing his old friends and acquaintances.

At this time he had become much interested in the language of ancient Egypt, and was acquiring considerable facility in the reading and interpretation of hieroglyphic inscriptions. In this connexion may be quoted a passage from a letter dated December

12th, 1904, where, writing about the Sarcophagus of Seti I. in the Soane Museum, he says: "It is a real misfortune that the sarcophagus is placed where it cannot be photographed, because the old engravings of Egyptian monuments frequently exhibit mistakes in the hieroglyphic texts, but even the scribes and sculptors of the ancient dynasties were by no means impeccable in that respect, as I found when transliterating and translating the stele of Menthusa." Until rheumatism disabled him, he was an expert draughtsman and calligraphist, a fair game-shot, and an enthusiastic angler.

Although in reality a delightful companion endowed with unusual conversational powers and a keen appreciation of literary and artistic culture, Greville Williams possessed a sensitive and modest temperament which tended, especially in his later years, to isolate him from his fellows. He was, perhaps, rather more nervous about his state of health than he need have been, and in consequence, withdrew almost entirely from scientific and social intercourse. It may likewise be considered that his straitened circumstances tended in the same direction, particularly as they debarred him from continuing his researches in pure chemistry. Whenever the conditions of his daily life allowed him leisure and opportunity for original inquiry, he was an enthusiastic worker, possessed of the true chemical instinct and a general scientific aptitude, as well as a large measure of manipulative dexterity and invention. It ought to be added that Greville Williams was a most interesting correspondent, and, having a happy knack of versifying, often passed from prose into poetry in letters addressed to his more intimate friends. Two epistles of this order are at the present moment before the writer. One of these, dated March 1st, 1861, deals in a playful way with the deceitfulness of unsupported spectrum observations, the later epistle, written a quarter of a century afterwards (August 20th, 1885), includes some humorous verses on a literary topic.

Most of Greville Williams's research work was concerned with certain groups of hydrocarbons and of volatile bases produced in the destructive distillation of organic substances, including combustible shales and coals. He made, however, a few incursions into mineral chemistry, especially in reference to peculiarities in the composition of the variety of beryl known as emerald.

Two discoveries of unusual interest were made by Greville Williams. One of these was the isolation of the most remarkable of the pentinenes, namely, isoprene (*Phil. Trans.*, 1860, **150**, 241). Of this hydrocarbon he determined the physical constants with accuracy; it has risen in importance since its polymerisation * into

* See the memoir just cited for an intimation as to such a change.

caoutchouc has been achieved, and since it has been obtained from terpene. In this connexion it is of interest to remember that Greville Williams ascertained that caoutchouc and terpene absorbed the same proportion of bromine. The other chief result of Williams's work was obtained in the study of quinoline bases, when he discovered cyanine or quinoline-blue (*Trans. Roy. Soc. Edin.*, 1856, **31**, 377). This substance, $C_{29}H_{35}N_2I$, was the first of the quinoline dyestuffs to be prepared. Some of these beautifully crystallised compounds have met with considerable application in photography as special sensitisers, but none of them is even tolerably fast to light.

Among the basic constituents present in certain kinds of tars from shales and coals, and in the products derived from the destructive distillation of cinchonine in the presence of potash, Greville Williams recognised and isolated several important bases. Pyridine was one of these; so also was a lutidine, perhaps a mixture of two or more of the nine possible lutidines, as well as a collidine, or a mixture of two or more of the twenty-two possible collidines; all these were found in coal tar, in Dorset shale tar, and in the distillate from cinchonine. Quinoline or leucoleine, discovered by Runge, was first thoroughly investigated by Williams (*Journ. Chem. Soc.*, 1863, **16**, 375). Some of the members of this series of bases are of great practical importance in the synthesis of certain medicinal preparations; γ -methylquinoline was first obtained by Williams from cinchonine, and named lepidine (b. p. 257°); it is thought to be identical with his iridoline from coal tar. He also described, under the name of cryptidine (b. p. 274°), one of the dimethylquinolines—perhaps the 2:3- or the 3:4-dimethylquinoline of Behrend.

Much useful work was accomplished by Greville Williams in connexion with the platinum compounds of the volatile bases which he examined. Some of his results were given in memoirs already named or were discussed in notes appearing in the *Philosophical Magazine* for September, 1854, and in the *Chemical Gazette* for August 16th, and September 1st and 15th, 1858. His determinations of vapour density were distinguished for the care and precision with which they were performed: these and other constants of many organic compounds were first accurately determined by him.

To about a score of memoirs and notes on organic bases which are credited to Greville Williams in the Royal Society's Catalogue of Scientific Papers, there must be added about fifteen devoted to hydrocarbons. And during the period 1882–1885, half a dozen inquiries of a technical character, connected with coal-gas and its

manufacture, were carried out and reported upon, mainly in the *Journal of Gas Lighting*.

Greville Williams made, as before stated, a few incursions into the domain of mineral chemistry. Chief among these were his researches on beryls and emeralds which appeared in the *Proceedings of the Royal Society* during 1873 and 1877 (21, 409; 26, 165). The earlier of these papers was devoted mainly to problems connected with the colour of the emerald, but included an account of experiments on the fusion of beryl, quartz, and sapphire by means of the oxy-hydrogen blowpipe. The precautions necessary to secure clear beads of these substances were defined, while the lowering of density by their passage into the vitreous state was accurately recorded. In the second memoir the chief method in use for effecting a separation between glucina (beryllia) and alumina was critically examined and greatly improved.

Two class-books were written by Greville Williams. The more important of these was published in 1857 under the title *A Handbook of Chemical Manipulation*. It contains 407 illustrations, with an appendix of twenty useful tables: a supplement dealing with more recently devised apparatus and methods was brought out in 1879. The other class-book was a *Manual of Chemical Analysis for Schools*, which appeared in 1858. He also wrote numerous articles for Ure's *Dictionary of Arts, Manufactures, and Mines*, for Watts's *Dictionary of Chemistry*, and for King's *Treatise on Coal Gas*. His contributions were clear and exact, while in his accounts of materials and operations his personal experience was largely drawn upon.

In June, 1862, Greville Williams was elected to the Fellowship of the Royal Society; he outlived the rest of the distinguished "fifteen" of that year. It was in 1862 also that he joined the Chemical Society. On November 25th, 1852, he married Henrietta Bosher, who died on February 16th, 1904. One son and three daughters survive.

The writer of this memorial notice has lost a friend of nearly sixty years' standing—a friend of rare quality and of high Christian character.

A. H. C.

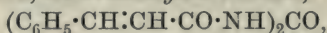
LXIX.—*Chemical Constitution and Hypnotic Action. Acid Amides and Products of the Condensation of Malonamides and Malonic Esters.*

By FREDERIC GEORGE PERCY REMFRY.

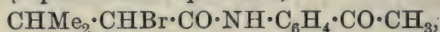
THE original idea of the work described in this paper was to study the changes in hypnotic effect produced by substituting the hydrogen of the amido-group in acid amides by various radicles. The physiological testing of the compounds was carried out by Dr. H. H. Dale at the Wellcome Physiological Research Laboratories, to whom the author desires to express his thanks. It may be at once mentioned that not one of these substances possessed any hypnotic properties whatever, and consequently the object of the investigation was not attained. The inactivity of these compounds is, at first sight, surprising, in view of the number of alkyl groups contained in some of them, and it is therefore probable that they are insoluble in lipoid substances, and that this—in the sense of the Overton-Meyer hypothesis—is responsible for their inactivity.

Many acid amides have already been tested physiologically (Nebenthan, *Arch. exp. Path. Pharm.*, 1895, **36**, 451), and have been found to be, in general, of weak hypnotic power, at the same time producing cramps similar to those induced by ammonia. The latter effect is found to be increased by substituting the hydrogen of the amido-group by alkyl radicles, but the narcotic power of the drug is thereby lessened. Consequently, in the present work only such substances, as a rule, were used for substituents as are already known to possess hypnotic properties of their own in some degree.

The four substances, *dicinnamoylcarbamide*,



ethyl cinnamoylcarbamate, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, *cinnamoyl-p-aminoacetophenone*, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3$, and *α-bromoisovaleryl-p-aminoacetophenone*,



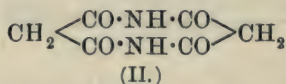
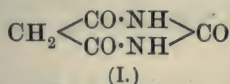
can be regarded as acid amides in which one hydrogen of the amido-group has been displaced by a radicle which (except in the first instance) is known to have hypnotic properties, and yet the resulting products were absolutely inactive.

Several substances of the type
$$\text{R} > \text{C} < \begin{matrix} \text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4 \\ \text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4 \end{matrix} \quad (\text{R} = \text{alkyl})$$

were prepared, but were found to be useless owing to their almost complete insolubility in all solvents.

The next step led to some interesting results on the effect produced on the general properties of ethyl malonate and malonamide by the introduction of various alkyl radicles, as will be explained later.

It is well known that it is necessary to introduce two ethyl groups into the molecule of barbituric acid (I) in order to impart to it its narcotic power, a methylethyl or ethyl group, or two methyl groups being insufficient. From this it was thought probable that the introduction of more than two ethyl groups into a somewhat similarly constituted molecule would still further increase the hypnotic effect. With this in view, condensation between malonamide and ethyl malonate was brought about by means of sodium ethoxide, a cyclic compound, *malonylmalonamide* (II), being formed :

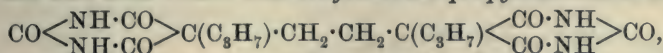


The formation of this compound is similar to that of the dialkylbarbituric acids from carbamide and ethyl alkylmalonates (Fischer and Dilthey, *Annalen*, 1904, **335**, 334), and from dialkylmalonamides and ethyl carbonate (D.R.-P. 163136). The general properties of this compound are also in agreement with those that would be expected of a substance having such a formula.

A number of alkyl derivatives of this substance have been prepared by direct alkylation; none of them, however, possessed any hypnotic properties, although resembling diethylbarbituric acid (veronal) structurally to some extent.

An analogous case to this is to be found in a recent paper by Rosenmund (*Ber.*, 1909, **42**, 4470), where the preparation of diketodiethylpiperazine, $\text{CEt}_2 \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{array} \text{CH}_2$, is described. This substance closely resembles diethylbarbituric acid, but possesses no hypnotic properties whatever; neither were any observed when four alkyl radicles were introduced, as in 3:6-diketo-2:5-dimethyl-2:5-diethylpiperazine, $\text{CMeEt} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{array} \text{CMeEt}$.

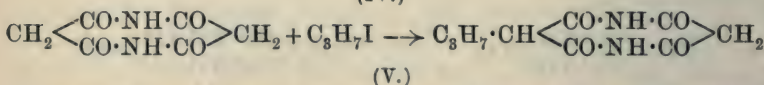
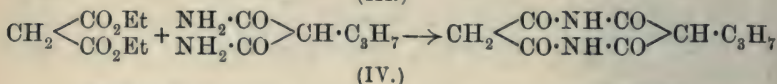
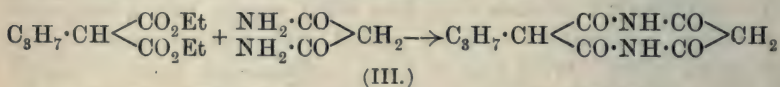
It has now been found that *ethylenebis-5-propylbarbituric acid*,



which may be regarded as two molecules of monopropylbarbituric acid joined together by an ethylene linking, was also quite inactive.

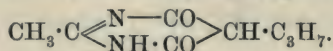
With the idea of proving the constitution of the different compounds obtained by alkylating malonylmalonamide, it was first ascertained, by heating with hydriodic acid to 300° according to

the Herzig-Meyer method, that all the alkyl groups were directly attached to carbon. Various condensations between alkyl substituted malonic esters and amides were then carried out, and it was expected that both the condensation products of, for example, (III), ethyl propylmalonate and malonamide, and (IV), ethyl malonate and propylmalonamide, would give one and the same product as (V), namely, that obtained by the introduction of one propyl radicle into malonylmalonamide, thus:

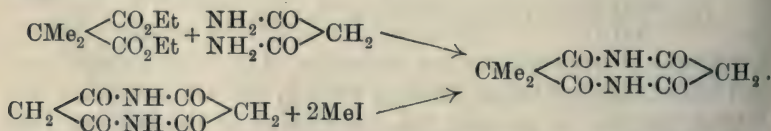


The product, *propylmalonylmalonamide*, obtained by propylating malonylmalonamide according to reaction (V), proved to be identical with the condensation product of ethyl propylmalonate and malonamide, as shown by reaction (III), and it is therefore clear that the alkyl radicle in the former reaction attaches itself to one of the methylene groups.

The condensation, however, of ethyl malonate and propylmalonamide did not proceed as depicted above in reaction (IV), but resulted in the production of a compound which proved, on analysis, to contain one molecule of carbon dioxide less than propylmalonylmalonamide, and which, from considerations to be given later, was considered to be 4:6-diketo-2-methyl-5-propyltetrahydropyrimidine,

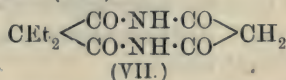
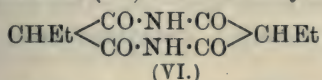


It now remained to ascertain the position of the two other alkyl groups which it was found possible to introduce into the molecule of malonylmalonamide. That of the second was proved in the following way. Ethyl dimethylmalonate and malonamide, when condensed together, were found to give a compound identical with that obtained when two methyl groups are introduced into malonylmalonamide, thus:

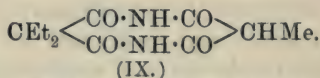
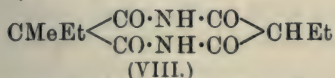


It could not be proved by a similar experiment that two ethyl or propyl groups enter the malonylmalonamide molecule in the same

way as the two methyl groups, owing to the condensation between ethyl diethyl- (or dipropyl-) malonate and malonamide proceeding in a different manner from that occurring in the case of ethyl dimethylmalonate. Proof, however, that the higher alkyl groups attach themselves in a similar manner to the methyl groups was obtained as follows. There are two possible formulæ for the *diethylmalonylmalonamide* obtained by ethylation, namely, the symmetrical (VI) and the unsymmetrical (VII):

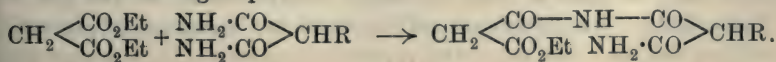


These, on methylation, will yield respectively *methylethylmalonylethylmalonamide* (VIII) and *diethylmalonylmethylmalonamide* (IX):

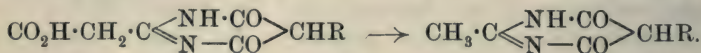


Now the product of condensation of ethyl methylethylmalonate and malonamide is *methylethylmalonylmalonamide*, and yields, on ethylation, *methylethylmalonylethylmalonamide*. This is not identical with the substance obtained by methylation of diethylmalonylmalonamide, which must, therefore, have a formula represented by (VII), and is diethylmalonylmalonamide. It has already been mentioned that when ethyl malonate was condensed with propylmalonamide, the reaction did not proceed as when using malonamide itself, but resulted in the formation of a pyrimidine derivative. Further experiments showed that in every case where an alkyl substituted malonamide of the type $\text{NH}_2 \cdot \text{CO} \cdot \text{CHR} \cdot \text{CO} \cdot \text{NH}_2$ was condensed with ethyl malonate or ethyl monoalkylmalonate, a similar pyrimidine ring was formed, an increase in size of the substituting group from methyl to propyl having apparently no further influence on the course of the reaction. Now Fischer and Dilthey (*Ber.*, 1902, **35**, 844) have shown that the formation of malonamides increases in difficulty progressively with the size and number of alkyl groups introduced into the molecule of ethyl malonate. This clearly shows that the character of malonamide must be greatly changed by the entrance of alkyl groups, and accounts for the variation in the course of the reaction when condensing ethyl malonate with alkylmalonamides in place of malonamide itself.

The course of the condensation in the formation of pyrimidines is probably as follows. Condensation first takes place between one ester and amido-group:

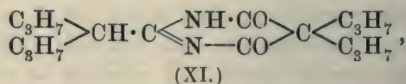
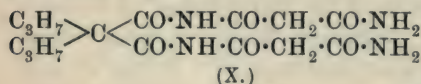


Water is then split off with closing of the ring, and hydrolysis of the remaining ester, and subsequent elimination of carbon dioxide, next occurs:



A similar loss of carbon dioxide, due to the action of sodium ethoxide, was observed by Einhorn (*Annalen*, 1908, **359**, 145), who found that the anhydride of diethylmalonic acid, when thus treated, gave ethyl diethylmalonate, ethyl hydrogen diethylmalonate, and ethyl diethylacetate.

The condensation of malonamides with malonyl chlorides leads to results similar to those obtained with the esters. In the case of the unsubstituted malonamide, a normal condensation product is obtained, but dialkylmalonamides again yield condensation products, from which carbon dioxide has been eliminated. Thus dipropylmalonyl chloride and malonamide (2 mols.) give *dipropylmalonyldimalonamide* (X), whilst the same acid chloride and dipropylmalonamide give 4:6-diketo-5:5-dipropyl-2- α -propylbutyltetrahydropyrimidine (XI):



the formation of the latter being analogous to that of the pyrimidine depicted in the last equation.

It has now been shown that an eight-membered ring is not formed when malonic ester or a substituted malonic ester is condensed with a substituted malonamide, but only when it is condensed with malonamide itself. Even the latter reaction, however, has its limits, malonamide condensing readily only with monoalkyl- and dimethyl-malonic esters. With methylethylmalonic esters it condenses to the eight-membered ring only with difficulty, and with diethyl- and higher dialkyl-malonic esters condensation takes place with the formation of substances which have entirely different properties from either the malonylmalonamide or pyrimidine compounds.

In this connexion the results of Meyer (*Ber.*, 1906, **39**, 198) on the influence of the size of alkyl groups on the formation of amides from malonic esters are of interest. He shows that in a disubstituted malonic ester at least two ethyl groups, either in the esters or attached to the quaternary carbon atom, are necessary to prevent reaction between the ester and aqueous ammonia. In the present

case, at least two ethyl groups, attached to the quaternary carbon atom only, are necessary to prevent a normal condensation with malonamide, the alkyl groups forming the esters apparently having no influence on the course of the reaction.

EXPERIMENTAL.



Ethyl malonate (1 mol.) and malonamide ($1\frac{1}{4}$ mols.), together with sodium (4 atoms) dissolved in twenty times its weight of absolute alcohol, were heated under pressure in a soda-water bottle for five hours in a brine-bath at $105-107^\circ$. When cold, the contents of the bottle were poured on a filter, and the colourless residue, after being washed with absolute alcohol, was dissolved in as little water as possible, and the solution just acidified by careful addition of concentrated hydrochloric acid. A colourless solid at once began to separate, and precipitation was complete in the course of a few hours. The solid was collected, washed with water, and crystallised from hot water. Colourless, crystalline, nodular masses were obtained, which melted and decomposed at $252-253^\circ$, after drying at 110° .

The alcoholic filtrate from the reaction mass was evaporated to dryness on the water-bath, the residue dissolved in a little water, and, on acidifying, a certain amount of colourless solid was precipitated. The yield in this case amounted to about 30 per cent. of the theoretical after crystallisation. When, however, substituted malonic esters or malonamides were employed, the yield decreased rapidly, and in many cases was very poor indeed.

In all condensations of this type, which are described later, the method employed was identical with this one. No details will, therefore, be necessary in future cases:

0.1106 gave 0.1720 CO_2 and 0.0366 H_2O . $\text{C}=42.4$; $\text{H}=3.7$.

0.1200 „ 16.2 c.c. N_2 at 19° and 784 mm. $\text{N}=16.4$.

1.1707 (air-dried) lost 0.2018 at 110° . $\text{H}_2\text{O}=20.8$.

$\text{C}_6\text{H}_6\text{O}_4\text{N}_2$ requires $\text{C}=42.36$; $\text{H}=3.53$; $\text{N}=16.5$ per cent.

$\text{C}_6\text{H}_6\text{O}_4\text{N}_2 \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=18.8$ per cent.

This substance is readily soluble in alcohol or acetone, moderately so in hot, but practically insoluble in cold, water. Dilute alkali hydroxides immediately dissolve it, the compound being reprecipitated unchanged by the addition of acids.

The sodium salt is a pink, crystalline substance, and is obtained on mixing alcoholic solutions of malonylmalonamide and sodium hydroxide:

0.1957 gave 0.1240 Na_2SO_4 . $\text{Na} = 20.93$.

$\text{C}_6\text{H}_4\text{O}_4\text{N}_2\text{Na}_2$ requires $\text{Na} = 21.5$ per cent.

Dimethylmalonylmalonamide, $\text{CMe}_2 \begin{matrix} \text{CO} \cdot \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \cdot \text{CO} \end{matrix} \text{CH}_2$.

Ethyl dimethylmalonate (1 mol.), malonamide (1 mol.), and sodium (2 atoms), in absolute alcohol, were condensed as usual. From both the solid and the filtrate from the reaction mixture, a similar compound was obtained, which, after crystallisation from hot water, gave fine, colourless, needle-shaped crystals, melting at $206-207^\circ$:

0.1066 gave 0.1890 CO_2 and 0.0482 H_2O . $\text{C} = 48.36$; $\text{H} = 5.06$.

0.1458 ,, 18 c.c. N_2 at 21° and 746 mm. $\text{N} = 14.1$.

$\text{C}_8\text{H}_{10}\text{O}_4\text{N}_2$ requires $\text{C} = 48.5$; $\text{H} = 5.05$; $\text{N} = 14.1$ per cent.

Dimethylmalonylmalonamide can also be prepared by acting on a dilute alcoholic solution of the sodium salt of malonylmalonamide with excess of methyl iodide exactly as described later in the formation of diethylmalonylmalonamide.

Methylethylmalonylmalonamide.

The quantities employed and the method of condensation were the same as in the last case, but the results were rather different. The alcoholic filtrate from the reaction mass, on treatment as usual, gave an oil, which slowly became crystalline, and, after recrystallisation from alcohol, was obtained in colourless needles, melting at $169-170^\circ$:

0.1194 gave 0.2242 CO_2 and 0.0604 H_2O . $\text{C} = 51.2$; $\text{H} = 5.66$.

0.1354 ,, 16 c.c. N_2 at 17° and 750 mm. $\text{N} = 13.8$.

$\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2$ requires $\text{C} = 50.9$; $\text{H} = 5.7$; $\text{N} = 13.2$ per cent.

The solid substance collected from the reaction mixture under the usual treatment gave a light yellow solid, which crystallised in colourless, nodular masses from a large volume of hot water. This compound does not melt, but burns completely when heated on platinum foil:

0.1098 gave 0.1850 CO_2 and 0.0412 H_2O . $\text{C} = 45.9$; $\text{H} = 4.2$.

0.1198 ,, 19.2 c.c. N_2 at 18° and 770 mm. $\text{N} = 19.2$.

$\text{C}_{14}\text{H}_{15}\text{O}_7\text{N}_5$ requires $\text{C} = 46.0$; $\text{H} = 4.1$; $\text{N} = 19.2$ per cent.

It has quite different properties from those of methylethylmalonylmalonamide, and evidently does not contain the malonylmalonamide ring.

Diethylmalonylmalonamide.

Sodium (2 atoms) was dissolved in thirty times its weight of alcohol, finely powdered malonylmalonamide (1 mol.) added, and the solution heated on the water-bath. The sodium compound which was formed, being insoluble in alcohol, was brought into solution by the cautious addition of water. Ethyl iodide (3 mols.) was then added slowly, and boiling was continued for three hours. Excess of alcohol was removed, and, on cooling, a colourless solid separated; this was collected, dissolved in hot water, and precipitated by the addition of dilute hydrochloric acid. The precipitate was washed with water, and crystallised from dilute alcohol, when colourless prisms, melting at $175-176^{\circ}$, were obtained. On acidifying the original mother liquors with hydrochloric acid, a gelatinous mass was precipitated, which slowly became crystalline. On recrystallisation from dilute alcohol, colourless prisms, melting at $175-176^{\circ}$, identical with the above, were obtained. The total yield was about equal to the weight of malonylmalonamide taken, by far the larger portion being furnished by the acidified mother liquors. This substance is readily soluble in alcohol, acetone, or ether, moderately so in hot, and insoluble in cold, water. It is dissolved by alkali hydroxides, and is reprecipitated by acids unchanged:

0.1287 gave 0.2516 CO_2 and 0.0743 H_2O . $\text{C}=53.3$; $\text{H}=6.4$.

0.1778 „ 19.0 c.c. N_2 at 14° and 744 mm. $\text{N}=12.5$.

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{C}=53.1$; $\text{H}=6.2$; $\text{N}=12.4$ per cent.

The *sodium* salt crystallises from alcohol in colourless needles:

0.2022 (air-dried) gave 0.0556 Na_2SO_4 . $\text{Na}=8.9$.

0.2390 „ lost 0.0074 at 120° . $\text{H}_2\text{O}=3.1$.

$\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}_2\text{Na}, \frac{1}{2}\text{H}_2\text{O}$ requires $\text{Na}=8.9$; $\text{H}_2\text{O}=3.5$ per cent.

Dimethylmalonylmethylmalonamide, $\text{CMe}_2 \begin{matrix} \text{CO} \cdot \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \cdot \text{CO} \end{matrix} \text{CHMe}$.

This was obtained by acting on a solution of dimethylmalonylmalonamide in dilute sodium hydroxide with methyl sulphate in the cold in the usual manner. The solid which separated out was collected, washed with water, and crystallised from benzene. It forms colourless needles, melting at 133° :

0.1140 gave 0.2146 CO_2 and 0.0584 H_2O . $\text{C}=51.3$; $\text{H}=5.74$.

0.1464 „ 16 c.c. N_2 at 17° and 772 mm. $\text{N}=13.2$.

$\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2$ requires $\text{C}=50.9$; $\text{H}=5.7$; $\text{N}=13.2$ per cent.

Diethylmalonylmethylmalonamide.

This was prepared from diethylmalonylmalonamide in the same manner as the last substance. The resulting crystalline precipitate was washed with water and crystallised from dilute acetic acid, when long, colourless prisms, melting at 118—119°, were obtained:

0.1074 gave 0.2156 CO₂ and 0.0639 H₂O. C=54.6; H=6.6.

0.1158 „ 12.3 c.c. N₂ at 20° and 750 mm. N=12.3.

C₁₁H₁₆O₄N₂ requires C=55.0; H=6.7; N=11.6 per cent.

Methylethylmalonylethylmalonamide.

The interaction of ethyl sulphate and methylethylmalonylmalonamide proceeded very slowly, and nothing separated out. The solution was acidified and extracted with ether, and a colourless oil was obtained, which slowly crystallised, and, after recrystallisation from xylene, gave colourless, prismatic needles, melting at 148—149°:

0.1029 gave 0.2078 CO₂ and 0.0598 H₂O. C=55.0; H=6.45.

C₁₁H₁₆O₄N₂ requires C=55.0; H=6.7 per cent.

All these three last-mentioned substances are soluble in alkali hydroxides, but efforts at further methylation were attended with no success.

Diethylmalonylethylmalonamide.

A warm solution of diethylmalonylmalonamide in sodium hydroxide was treated with ethyl sulphate in the usual way. The solid obtained on acidifying proved to be mostly unchanged diethylmalonylmalonamide, with very little of the ethylated product. This was obtained, after several crystallisations from dilute acetic acid, in straw-coloured plates, melting at 88—89°.

Boiling an alcoholic suspension of the sodium salt of diethylmalonylmalonamide with sodium ethyl sulphate gave no better yield, and all attempts to obtain a tetraethyl compound were unsuccessful:

0.1196 gave 0.2484 CO₂ and 0.0771 H₂O. C=56.64; H=7.2.

C₁₂H₁₈O₄N₂ requires C=56.7; H=7.1 per cent.

Dipropylmalonylmalonamide.

The reaction was carried out exactly as in the case of the diethyl compound. The compound crystallises from dilute acetic acid in colourless needles, melting at 209—210°:

0.1182 gave 0.2448 CO₂ and 0.0778 H₂O. C=56.4; H=7.37.

0.1335 „ 13.4 c.c. N₂ at 23° and 762 mm. N=11.7.

C₁₂H₁₈O₄N₂ requires C=56.7; H=7.1; N=11.0 per cent.

Propylmalonylmalonamide.

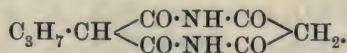
The original mother liquors from the last-mentioned substance were acidified, the resulting precipitate collected, washed with water, and crystallised from acetic acid, when colourless prisms, melting at 188—189°, were obtained :

0·1107 gave 0·2057 CO₂ and 0·0582 H₂O. C=50·7; H=5·9.

0·1254 „ 14 c.c. N₂ at 17° and 745 mm. N=13·0.

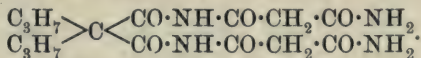
C₉H₁₂O₄N₂ requires C=50·9; H=5·7; N=13·2 per cent.

The empirical formula corresponds with the introduction of only one propyl radicle into the molecule of malonylmalonamide, and is thus represented by the formula :



Proof of the correctness of this is afforded by the fact that when ethyl propylmalonate is condensed in the usual way with malonamide, a substance is obtained which is identical in all respects with the above compound.

Dipropylmalonyldimalonamide,



Dipropylmalonyl chloride (1 mol.) and malonamide (2 mols.) were well mixed in a flask furnished with an air condenser, and heated in an oil-bath at 110—120° for seven hours. Three times the volume of benzene was then added, and boiling continued for an hour, after which the hot benzene was decanted, and the residue dried under diminished pressure at 100°. It was then extracted several times with hot water. This substance, being insoluble in all the usual organic solvents and water, could not be obtained in a crystalline form, but only as a colourless powder :

0·1013 gave 0·1870 CO₂ and 0·0560 H₂O. C=50·35; H=6·2.

0·1330 „ 18·2 c.c. N₂ at 17° and 748 mm. N=15·9.

C₁₅H₂₄O₆N₄ requires C=50·57; H=6·7; N=15·7 per cent.

Condensation of Ethyl Diethylmalonate and Malonamide.

The ester (1 mol.), the amide (1 mol.), and sodium (3 atoms) were condensed in the usual way. On acidifying the aqueous solution of the solid part of the reaction mixture, a pale yellow, amorphous solid was precipitated. All attempts at obtaining this substance in a crystalline form were fruitless, it being extremely insoluble in organic solvents and water. The mother liquors from the above compound slowly deposited colourless, prismatic crystals,

which were recrystallised from hot water. This substance has no melting point, but burns completely when heated on platinum foil:

0.1000 gave 0.1598 CO₂ and 0.0388 H₂O. C=43.58; H=4.33.

0.0954 „ 19.5 c.c. N₂ at 21° and 760 mm. N=23.9.

C₁₇H₂₀O₈N₈ requires C=43.9; H=4.3; N=24.1 per cent.

Condensation of Methyl Diethylmalonate and Malonamide.

The methyl ester was here substituted for the ethyl ester. This, however, had no effect on the course of the reaction, and the crystalline product was identical with that obtained in the last case:

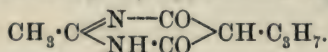
0.1128 gave 0.1792 CO₂ and 0.0406 H₂O. C=43.34; H=4.03.

0.1051 „ 0.1658 CO₂ „ 0.0394 H₂O. C=43.02; H=4.2.

0.1270 „ 25.9 c.c. N₂ at 17° and 768 mm. N=24.4.

C₁₇H₂₀O₈N₈ requires C=43.9; H=4.3; N=24.1 per cent.

4: 6-Diketo-2-methyl-5-propyltetrahydropyrimidine,



Propylmalonamide (1 mol.), ethyl malonate (1 mol.), and sodium (3 atoms) were condensed and worked up as usual. The product crystallised from acetic acid in colourless needles, which did not melt at 300°. They are insoluble in dilute hydrochloric acid, hot or cold, but readily soluble in cold dilute sodium hydroxide:

0.1183 gave 0.2482 CO₂ and 0.0802 H₂O. C=57.2; H=7.5.

C₈H₁₂O₂N₂ requires C=57.1; H=7.1 per cent.

4: 6-Diketo-5-methyl-2-ethyltetrahydropyrimidine.

Prepared from methylmalonamide and ethyl methylmalonate in the same manner as the last substance. The compound crystallises from acetic acid in clusters of colourless, prismatic needles, which do not melt at 300°:

0.1145 gave 0.2265 CO₂ and 0.0694 H₂O. C=53.9; H=6.7.

0.1002 „ 15.4 c.c. N₂ at 15° and 748 mm. N=18.1.

C₇H₁₀O₂N₂ requires C=54.4; H=6.5; N=18.2 per cent.

4: 6-Diketo-5-ethyl-2-propyltetrahydropyrimidine.

Prepared from ethylmalonamide and ethyl ethylmalonate. The compound crystallises from dilute acetic acid in colourless, needle-shaped prisms, which do not melt at 300°:

0.1311 gave 0.2860 CO₂ and 0.0904 H₂O. C=59.5; H=7.6.

0.1160 „ 15 c.c. N₂ at 22° and 770 mm. N=15.3.

C₉H₁₄O₂N₂ requires C=59.3; H=7.7; N=15.4 per cent.

4 : 6-Diketo-5-propyl-2-butyltetrahydropyrimidine.

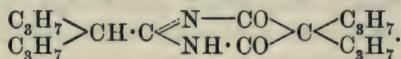
Prepared from propylmalonamide and ethyl propylmalonate. It crystallises from dilute acetic acid in small, colourless prisms, not melting at 300°:

0·1352 gave 0·3082 CO₂ and 0·1032 H₂O. C=62·1; H=8·5.

0·1314 „ 15 c.c. N₂ at 25° and 770 mm. N=13·3.

C₁₁H₁₈O₂N₂ requires C=62·9; H=8·6; N=13·3 per cent.

4 : 6-Diketo-5 : 5-dipropyl-2- α -propylbutyltetrahydropyrimidine,



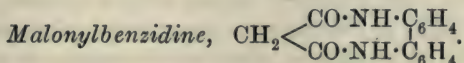
This substance was prepared in a different way from the foregoing pyrimidine derivatives. Equimolecular quantities of dipropylmalonamide and dipropylmalonyl chloride were heated together on the water-bath for sixteen hours, care being taken to exclude moisture. The resulting yellow, jelly-like substance was washed with water and pressed on porous plate. When dry, it was dissolved in cold benzene, in which it is readily soluble, filtered from some insoluble matter, the benzene removed by evaporation, and the residue crystallised from acetic acid. Fine, long, colourless needles were obtained, which melt at 130—131°.

This compound is insoluble in both sodium hydroxide and hydrochloric acid, whether dilute, strong, cold or hot:

0·1096 gave 0·2778 CO₂ and 0·1024 H₂O. C=69·1; H=10·3.

0·1212 „ 9·7 c.c. N₂ at 20° and 763 mm. N=9·43.

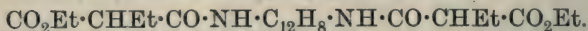
C₁₇H₃₀O₂N₂ requires C=69·4; H=10·2; N=9·5 per cent.



Equimolecular quantities of ethyl malonate and finely powdered benzidine were heated together, in a flask provided with an air condenser, in a metal-bath at 210—220°. As soon as the ethyl malonate began to boil, alcohol could be detected escaping from the condenser. In a short time a solid commenced to separate in the flask, and soon the whole contents of the flask became solid. The condensation product proved to be practically insoluble in all the usual organic solvents and water. Any unchanged substance was removed by repeated extractions with boiling alcohol and acetone, and the bluish-grey residual powder finally heated at 100° to remove all traces of solvent:

0·1740 gave 0·4530 CO₂ and 0·0922 H₂O. C=71·0; H=5·9.

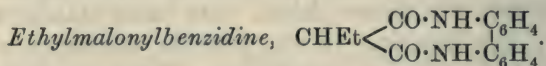
C₁₅H₁₂O₂N₂ requires C=71·4; H=4·76 per cent.

Di-α-carbethoxybutyrylbenzidine,

Ethyl ethylmalonate ($1\frac{1}{2}$ mols.) and benzidine (1 mol.) were heated together, as above, at $220-230^\circ$. In the course of about half an hour, the whole solution became a solid mass; this was crushed in a mortar, boiled with alcohol, and the whole filtered. The residue, when dry, did not melt at 300° . From the alcoholic filtrate, on cooling, three crops of a bluish-grey, flocculent solid were obtained. These were dissolved together in alcohol, filtered from some insoluble matter, and on slowly evaporating the filtrate, small, colourless, needle-shaped crystals were obtained, which melt at 189° , and are insoluble in dilute hydrochloric acid:

0.1280 gave 0.3146 CO_2 and 0.0796 H_2O . $\text{C}=67.0$; $\text{H}=6.9$.

$\text{C}_{26}\text{H}_{32}\text{O}_6\text{N}_2$ requires $\text{C}=66.6$; $\text{H}=6.8$ per cent.



The insoluble substance mentioned in the preparation of the last compound, which does not melt at 300° , was extracted several times with boiling acetone, and the residue dried at 100° :

0.1382 gave 0.3682 CO_2 and 0.0732 H_2O . $\text{C}=72.7$; $\text{H}=5.9$.

0.1236 „ 10 c.c. N_2 at 22° and 777 mm. $\text{N}=9.65$.

$\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{C}=72.9$; $\text{H}=5.7$; $\text{N}=10.0$ per cent.

Diethylmalonylbenzidine.

Prepared from equimolecular quantities of ethyl diethylmalonate and benzidine. The alcoholic extract of the resulting condensation product deposited a bluish-grey, amorphous substance, which was again dissolved in alcohol to effect purification. It melted sharply at 224° :

0.1149 gave 0.3122 CO_2 and 0.0645 H_2O . $\text{C}=74.1$; $\text{H}=6.3$.

$\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_2$ requires $\text{C}=74.0$; $\text{H}=6.5$ per cent.

Propylmalonylbenzidine.

This is a grey, amorphous substance, practically insoluble in boiling alcohol and other organic solvents. It decomposes at 298° :

0.1277 gave 0.3335 CO_2 and 0.0737 H_2O . $\text{C}=71.2$; $\text{H}=6.3$.

$\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C}=73.5$; $\text{H}=6.1$ per cent.

Dipropylmalonylbenzidine.

This is a bluish-grey, amorphous substance, which melts at 264° .

Ethyl Decane- $\delta\delta\eta\eta$ -tetracarboxylate,
 $C_3H_7 \cdot C(CO_2Et)_2 \cdot CH_2 \cdot CH_2 \cdot C(CO_2Et)_2 \cdot C_3H_7$.

This was prepared according to the method given by Lean (Trans., 1894, **65**, 1007) for the preparation of ethyl octane- $\gamma\gamma\zeta\zeta$ -tetracarboxylate ("ethyl diethylbutanetetracarboxylate"), the quantities used being 50 grams of ethyl butanetetracarboxylate (Perkin, Trans., 1894, **65**, 578), 6.6 grams of sodium in 80 grams of absolute alcohol, and 50 grams of propyl iodide. The ethereal extract left a clear brown oil, equal in weight to that of the ester taken, which crystallised on keeping. It was washed with light petroleum to remove any oil, and a pure substance was obtained without further crystallisation. On recrystallisation from dilute acetic acid, large, colourless, four-sided plates were obtained, which melted at 102—103°:

0.1286 gave 0.2892 CO_2 and 0.1032 H_2O . $C = 61.3$; $H = 8.98$.

$C_{22}H_{38}O_8$ requires $C = 61.4$; $H = 8.8$ per cent.

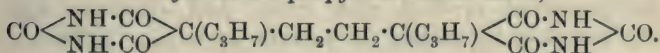
Decane- $\delta\delta\eta\eta$ -tetracarboxylic Acid.

This crystallises from acetic acid in fine, colourless needles, which melt and decompose at 228°:

0.1477 gave 0.2843 CO_2 and 0.0900 H_2O . $C = 52.5$; $H = 6.82$.

$C_{14}H_{22}O_8$ requires $C = 52.84$; $H = 6.9$ per cent.

Ethylenebis-5-propylbarbituric Acid,

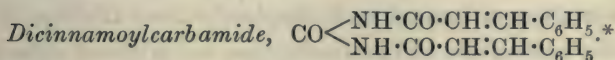


Ethyl decane- $\delta\delta\eta\eta$ -tetracarboxylate (1 mol.), carbamide (3 mols.), and sodium (6 atoms) were condensed and worked up in the same manner as the malonamide condensations. The colourless solid obtained was crystallised from alcohol, and gave needle-shaped crystals, which did not melt at 300°:

0.1234 gave 0.2394 CO_2 and 0.0734 H_2O . $C = 52.9$; $H = 6.6$.

0.1824 „ 23.4 c.c. N_2 at 22° and 767 mm. $N = 15.1$.

$C_{16}H_{22}O_6N_4$ requires $C = 52.5$; $H = 6.2$; $N = 15.3$ per cent.



A mixture of cinnamoyl chloride (2 mols.) and carbamide (1 mol.) was gently heated in an oil-bath. When the temperature in the

* During the course of this work some cinnamamide was required, and as no mention could be found in the literature of its formation having been attempted by means of the action of aqueous ammonia on the ester, some experiments were carried out in this direction. Five grams of ethyl cinnamate and 30 c.c. of

flask reached 100° , a vigorous reaction commenced, and hydrogen chloride was evolved. The reaction was soon over, and a solid mass remained, to which dry xylene was added, the mixture being heated to boiling for two hours. The hot xylene was then decanted, and the residue repeatedly extracted with boiling alcohol. A colourless powder was left, which was practically insoluble in all the usual organic solvents except acetic acid, from which it crystallised in clusters of small, colourless needles, which melted and decomposed at 246° :

0.1147 gave 0.3020 CO_2 and 0.0514 H_2O . $\text{C}=71.8$; $\text{H}=5.0$.

$\text{C}_{10}\text{H}_{14}\text{O}_3\text{N}_2$ requires $\text{C}=71.6$; $\text{H}=5.0$ per cent.

Ethyl Cinnamoylcarbamate, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$.

This substance has already been described by Diels and Heintzel (*Ber.*, 1905, **38**, 302), who prepared it by the action of ethyl cinnamate on ethyl sodiocarbamate. Whereas, however, the above authors obtained only 5 grams of crude product from 50 grams of ester, the method described here gives a yield of 48 per cent. of the cinnamoyl chloride used.

Cinnamoyl chloride (1 mol.) and urethane (2 mols.) were covered with dry benzene, which was heated to boiling for two hours. The benzene was then removed as far as possible by evaporation under diminished pressure, and the residue allowed to crystallise. Any unchanged urethane was extracted by vigorously stirring the dry, well-powdered product with water, and cinnamic acid was similarly removed by means of sodium carbonate solution. The residue was collected, washed well with water, and crystallised from dilute acetic acid. It formed colourless needles, melting at $108\text{--}109^{\circ}$. (Found, $\text{N}=6.5$. Calc., $\text{N}=6.4$ per cent.)

isoButyl Allophanate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$.

Cyanic acid, obtained by heating cyanuric acid, was bubbled through *isobutyl* alcohol kept cool by a freezing mixture. After passing gas for some time, the alcohol became cloudy, it was then filtered, and the filtrate allowed to evaporate spontaneously in the air. Crystals soon formed, and completely filled the liquid. They concentrated ammonia ($\text{D } 0.880$) were shaken from time to time in a closed bottle. For nearly three weeks no apparent change took place, and then crystals began slowly to form in the ethyl cinnamate layer. After two months it was found that 1.89 grams of pure cinnamamide had been formed, which is equal to a 45 per cent. yield. In three months the yield had risen to 60 per cent., and in four months to 70 per cent. A pure specimen was obtained in large, hexagonal plates, which melted at $148\text{--}148.5^{\circ}$ (corr.), the melting point given by Autenrieth (*Ber.*, 1901, **34**, 186) being 147° .

were collected and recrystallised from hot water, from which *isobutyl allophanate* separated in very fine, colourless needles, melting at 178—179°:

0.1708 gave 25.4 c.c. N_2 at 17° and 769 mm. $N = 17.8$.

$C_6H_{12}O_3N_2$ requires $N = 17.5$ per cent.

tert.-Amyl Allophanate, $NH_2 \cdot CO \cdot NH \cdot CO_2 \cdot CMe_2Et$.

Since preparing this compound, a description of its properties has appeared (D.R.-P. 226228). The melting point, however, is there given as 2° lower than that found by the author, namely, 151—152° (corr.), the substance decomposing a few degrees higher. The method of preparation was similar to that used in the case of *isobutyl allophanate*, except that the alcohol was not cooled, and the temperature allowed to rise to 70°.

Cinnamoyl-p-aminoacetophenone,
 $C_6H_5 \cdot CH : CH \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot CH_3$.

Equimolecular quantities of cinnamoyl chloride, *p*-aminoacetophenone, and dry powdered potassium carbonate were mixed in a flask provided with a reflux condenser, covered with dry xylene, and heated to boiling for three hours in an oil-bath. The xylene, when cold, was decanted, and the residue washed, first with cold alcohol, and then warm water. The crude *cinnamoyl-p-aminoacetophenone*, which was left undissolved, was crystallised from acetic acid, and obtained in small, colourless needles, melting at 204—205°:

0.1309 gave 0.3654 CO_2 and 0.0662 H_2O . $C = 76.2$; $H = 5.66$.

$C_{17}H_{15}O_2N$ requires $C = 76.6$; $H = 5.6$ per cent.

α -Bromoisovaleryl-p-aminoacetophenone,
 $CHMe_2 \cdot CHBr \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot CH_3$.

Equimolecular quantities of *α -bromoisovaleryl chloride*, *p*-aminoacetophenone, and dry powdered potassium carbonate were covered with dry benzene in a flask, and heated on the water-bath for an hour. After being kept at the ordinary temperature for twelve hours, the solution was filtered from inorganic matter, and evaporated to a small volume on the water-bath. On cooling, a mass of crystals separated, which, when collected and recrystallised from dilute acetic acid, formed colourless needles, melting at 113—114°:

0.1170 gave 0.2144 CO_2 and 0.0565 H_2O . $C = 50.0$; $H = 5.4$.

0.1614 „ 0.1037 AgBr. $Br = 27.3$.

$C_{13}H_{16}O_2NBr$ requires $C = 52.35$; $H = 5.36$; $Br = 26.85$ per cent.

THE WELLCOME CHEMICAL WORKS,
 DARTFORD, KENT.

LXX.—*The Resolution of Asymmetrical Derivatives of Phosphoric Acid.*

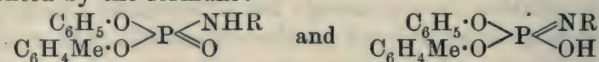
By FREDERIC STANLEY KIPPING and FREDERICK CHALLENGER, B.Sc.
(1851 Exhibition Scholar).

IN a paper which has just been published (*Ber.*, 1911, **44**, 356), Meisenheimer and Lichtenstadt have shown that methylethylphenylphosphine oxide exists in optically active forms. These authors claim, and rightly so, that they are the first to have obtained derivatives of phosphorus, of which the optical activity is conclusively proved to be exclusively due to the asymmetric distribution of the radicles around the phosphorus atom.

Not contented with their undoubted success, they pass on to criticise the experiments of Luff and Kipping on the resolution of asymmetric derivatives of phosphoric acid (*Trans.*, 1909, **95**, 1993); they suggest, not only that this investigation was based on some earlier work of Meisenheimer (*Ber.*, 1908, **41**, 3966), but also that its results were inconclusive, because, as Luff and Kipping's isomerides differed little in specific rotation, the isomerism was not proved to be due to the asymmetry of the molecules; they also suggest that the compounds in question are structurally, and not stereochemically, isomeric.

The priority claim is of small importance, but, as a matter of fact, experiments on the preparation and resolution of phosphorus compounds of the type $\text{POR}^1\text{R}^2\text{R}^3$ were carried out in these laboratories at least ten years ago, and some of the results were published in 1902 (Caven, *Trans.*, 1902, **81**, 1362); this paper was specifically referred to by Luff and Kipping (*loc. cit.*).

As regards Meisenheimer and Lichtenstadt's other criticisms, the point at issue is whether the isomeric substituted amides which are formed by the interaction of phenyl-*p*-tolylphosphoryl chloride and *l*-menthylamine, or *d*-hydrindamine, are structurally isomeric, as represented by the formulæ:



respectively, or whether they are optically isomeric derivatives of *d*- and *l*-phenyl *p*-tolyl hydrogen phosphates.

Meisenheimer and Lichtenstadt seem to attach importance to the fact that the two *d*-hydrindamides, and likewise the two *l*-menthylamides, are not widely different in specific rotation in methylalcoholic solution, and remark that "der grösste beobachtete Unterschied in den direkt abgelesenen Drehungswerten betrug weniger als

0.20°" How they arrive at the figure 0.20° from the published data is not very obvious, but in any case the fact that the isomerides differ only by about 5° in specific rotation is no argument one way or the other.* At the present time very little is known as to the relation between molecular rotation and chemical structure, and to premise that the *d*-hydrindamides or *l*-menthylamides of the enantiomorphously related phenyl *p*-tolyl hydrogen phosphates should show a greater difference in specific rotation than structurally isomeric compounds of the formulæ given above, is merely a gratuitous assumption. As an example of the impossibility of foretelling either qualitatively or quantitatively the specific rotations of such compounds, it may be noted that the *d*-hydrindamide of *d*-benzylmethylacetic acid is lævorotatory ($\alpha_D - 15.5^\circ$), whereas the *l*-menthylamide of the same acid is dextrorotatory ($\alpha_D + 7.5^\circ$) in methyl-alcoholic solution (Salway and Kipping, *Trans.*, 1904, **85**, 448).

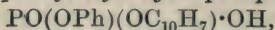
The only relevant criticism of Meisenheimer and Lichtenstadt is, in fact, that "Die Isomerie könnte sehr wohl auch auf Strukturverschiedenheit . . . zurückzuführen sein." This point was considered by Luff and Kipping (*loc. cit.*), but as the isomeric amides were found to be stable in presence of alkalis, it was concluded that they were not represented respectively by the formulæ given above; consequently, they were considered to be structurally identical and optically isomeric.

Although this conclusion seemed to be a sound one, the study of asymmetric derivatives of phosphoric acid was continued, and has been in progress during the last eighteen months, but has been frequently interrupted owing to the departure of the student who was taking part in the work. The results are now published—perhaps in a less complete state than would otherwise have been desirable—in consequence of the appearance of Meisenheimer and Lichtenstadt's paper, which renders unnecessary any further evidence of the existence of optically active phosphorus compounds of the type $\text{POR}^1\text{R}^2\text{R}^3$.

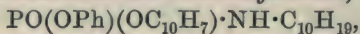
In the first place, as the previous failure to resolve phenyl *p*-tolyl hydrogen phosphate by the usual method might possibly be attributed to the similarity of the phenyl and *p*-tolyl radicles, it seemed advisable to prepare an asymmetric phosphoric acid in which the two hydrocarbon radicles would differ considerably in molecular weight. This was accomplished by treating phenylphosphoryl chloride with sodium β -naphthoxide, or with β -naphthol, and then hydrolysing the product.

* The *l*-menthylamides showed a difference of about 22° in molecular rotation, or a value which is actually about half that of the molecular rotation (in aqueous solution) of Meisenheimer and Lichtenstadt's oxide.

The *dl*-phenyl β -naphthyl hydrogen phosphate,



was then combined with various optically active bases, and the salts were fractionally crystallised, but in no case was there any sign that a resolution had occurred. It therefore seemed desirable to prove the asymmetry of the acid molecule and to attempt the resolution of the *dl*-compound by the method previously employed; for this purpose the chloride of the acid was treated with *l*-menthylamine. An examination of the *l*-menthylamide,



showed that it was a mixture of two isomeric amides; the more sparingly soluble component was easily isolated, but the more readily soluble one was not obtainable quite free from its isomeride. The fact that the pure acid chloride yields two *l*-menthylamides, just as phenyl-*p*-tolylphosphoryl chloride gives isomeric *l*-menthylamides and *d*-hydrindamides, establishes the asymmetry of the phosphoric acid, unless, of course, the amides are structurally different. This alternative is highly improbable; firstly, because both the *l*-menthylamides are stable in presence of alkalis; secondly, because a careful investigation of the *l*-menthylamide and hydrindamide of *d*-benzylmethylacetic acid (Salway and Kipping, *loc. cit.*) failed to reveal the existence of isomerides; and thirdly, because structural isomerism of the suggested type in the case of substituted amides, if known at all, is a very rare occurrence.

As, however, it might be argued that substituted amides derived from phosphoric acids are not comparable with those derived from carboxylic acids, some further evidence was perhaps desirable in favour of the view that the *l*-menthylamides are structurally identical. This evidence was obtained in the following manner: Phenyl- β -naphthylphosphoryl chloride was treated with ammonia, and also with *p*-toluidine; the *amide*, $\text{PO(OPh)(OC}_{10}\text{H}_7\text{)}\cdot\text{NH}_2$, and the *p*-toluidide, $\text{PO(OPh)(OC}_{10}\text{H}_7\text{)}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, which were thus obtained, and also the *di-p*-toluidide of phenyl dihydrogen phosphate, $\text{PO(OPh)(NH}\cdot\text{C}_6\text{H}_4\text{Me)}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, were carefully examined, but were found to show the properties of homogeneous products. It may be concluded therefore that the substituted amides of phosphoric acid do not exist in stable structurally isomeric forms, and that the existence of the isomeric *d*-hydrindamides and *l*-menthylamides of phenyl *p*-tolyl and of phenyl β -naphthyl hydrogen phosphates is due to the asymmetry of the molecules of these acids.

The readiness with which *dl*-phenyl *p*-tolyl and *dl*-phenyl β -naphthyl hydrogen phosphates are resolved into their optically active components by the fractional crystallisation of their sub-

stituted amides is in striking contrast to the behaviour of the salts of these acids; of the three amides which have been examined, all have given positive results, but of the twelve or more salts, not one has exhibited the least sign of a possible resolution. In this respect, judging from a footnote in Meisenheimer and Lichtenstadt's paper, and from a private communication from another source, the salts of the asymmetric phosphoric acids resemble those of the asymmetric phosphonium hydroxides. In neither case, however, does this negative evidence throw any doubt on the existence of the enantiomorphously related isomerides; as in so many instances on record, the separation of the optically active forms, if they are sufficiently stable, is probably merely a question of the fortuitous choice of a suitable base or acid, as the case may be.

EXPERIMENTAL.

Phenyl-β-naphthylphosphoryl Chloride, $\text{PO}(\text{OPh})(\text{OC}_{10}\text{H}_7)\text{Cl}$.

This compound was first prepared by gradually adding an ethereal solution of sodium β-naphthoxide (1 mol.) to an ethereal solution of phenylphosphoryl chloride (1 mol.), and then heating the mixture during about an hour; the sodium chloride was then removed by shaking the ethereal solution with water, and the product was ultimately isolated by fractional distillation under greatly diminished pressure.

It was afterwards found that an equally good result is obtained by mixing phenylphosphoryl chloride with β-naphthol in molecular proportions, and then gradually heating the mixture on a sand-bath until the evolution of hydrogen chloride ceases. The liquid is then fractionally distilled under diminished pressure, and the product, which passes over from about 280° to 300°/29 mm., is collected; from this preparation, by further fractional distillation, the pure chloride is obtained as a viscid, colourless liquid, which boils at about 286°/29 mm., and crystallises when it is cooled to atmospheric temperature, but melts again at relatively low temperatures.

For analysis, samples of the chloride were shaken with a concentrated solution of ammonium hydroxide, the precipitated phenyl-β-naphthylphosphoramide was separated by filtration, and the filtrate was treated with excess of silver nitrate and dilute nitric acid:

1.0544 gave 0.4926 AgCl. Cl=11.55.

1.0998 „ 0.5129 AgCl. Cl=11.53.

$\text{C}_{17}\text{H}_{12}\text{O}_3\text{ClP}$ requires Cl=11.19 per cent.

Phenyl-β-naphthylphosphoryl chloride is only very slowly hydrolysed even by hot water or by a cold solution of sodium carbonate;

nevertheless, it gradually decomposes on exposure to moist air, and then fumes strongly.

Phenyl β -Naphthyl Hydrogen Phosphate, $\text{PO}(\text{OPh})(\text{OC}_{10}\text{H}_7)\cdot\text{OH}$.

This acid may, of course, be obtained by warming the pure chloride with water for some time, but it may also be prepared directly from the crude product of the interaction of phenylphosphoryl chloride and β -naphthol. For this purpose, the oily liquid, which consists of a mixture of phenylphosphoryl chloride, phenyl- β -naphthylphosphoryl chloride, and phenyl di- β -naphthyl phosphate, is heated to about 60° , and is then vigorously shaken with a 15 per cent. aqueous solution of sodium hydroxide; the two chlorides are hydrolysed, and their sodium salts pass into solution, whilst the phenyl di- β -naphthyl phosphate separates in crystals.

When the solution of the sodium salts is directly treated with excess of hydrochloric acid, the phenyl β -naphthyl hydrogen phosphate, which is precipitated as an oil, slowly solidifies when it is rubbed, but it almost invariably separates again from solvents in an oily condition. For this reason, it is advisable to purify the rather sparingly soluble sodium salt by recrystallisation from water; the acid obtained from the purified sodium salt is then easily recrystallised from a mixture of benzene and light petroleum.

Phenyl β -naphthyl hydrogen phosphate separates from its solutions in colourless, microscopic, anhydrous needles, and melts at $92\text{--}93^\circ$. It is almost insoluble in water, and is only very sparingly soluble in light petroleum, but it dissolves freely in alcohol, benzene, or ethyl acetate. The acid was not analysed, but its equivalent was determined by titration with a solution of sodium hydroxide, and was found to be 298; the calculated value is 300. The composition of the acid was further established by the analyses of the derivatives, which are described later.

The *sodium* salt is relatively sparingly soluble in cold water, from which it separates in long, colourless needles. The *calcium*, *barium*, *zinc*, and *silver* salts are obtained by precipitation, and are sparingly soluble or insoluble in water. The *p-toluidine* salt crystallises well from aqueous alcohol in lustrous needles, and melts at $163\text{--}164^\circ$.

Quinine Phenyl β -Naphthyl Phosphate.

This salt was prepared by treating the sodium salt of the acid with a slight excess of quinine hydrochloride in aqueous solution; it was precipitated as an oil, which immediately solidified to a hard, crystalline mass. The crude product, which melted at about 170° , was systematically crystallised from a mixture of alcohol and ethyl

acetate, and after many operations the various fractions were examined; they all melted at 174—175°, except the most readily soluble one, which liquefied at about 170°.

The specific rotations of the two extreme fractions were determined in methyl-alcoholic solution, and were found to be identical:

0.1623, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 1.41^\circ$, whence $[\alpha]_D - 108.6^\circ$.

0.1903, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 1.65^\circ$, whence $[\alpha]_D - 108.4^\circ$.

The quinine salt is readily soluble in alcohol and benzene, but is only sparingly soluble in ethyl acetate and insoluble in ether; it crystallises in needles.

Strychnine Phenyl β -Naphthyl Phosphate.

The oily precipitate obtained by double decomposition in the usual manner was washed with water and kept during several weeks, but it did not crystallise, and it also separated as an oil from aqueous alcohol and aqueous acetone. When, however, it was heated at 100°, the oil gradually solidified, and the dry salt was easily crystallised from ethyl acetate to which a little methyl alcohol was added. The compound was fractionally crystallised from this solvent, but it underwent no change in melting point, and behaved like a homogeneous substance. The deposits consisted of rosettes of colourless needles, which melted at 142—143°, and seemed to contain solvent, as they immediately liquefied and gave a frothy mass when they were suddenly heated at about 137°.

The strychnine salt is only sparingly soluble in boiling ethyl acetate and in boiling water, but it dissolves freely in chloroform, alcohol, or acetone.

Cinchonidine Phenyl β -Naphthyl Phosphate.

The precipitated salt was a viscid oil, but it crystallised in a few minutes; when washed with water and dried, the crude product melted at about 190—195°, but after recrystallisation from aqueous methyl alcohol, its melting point rose to 196—197°. The compound was fractionally crystallised from this solvent, and the extreme fractions were then compared; the "most sparingly soluble" one melted at 196—197°, and the "most readily soluble" one at 195—197°. The salt was also repeatedly crystallised from a mixture of chloroform and light petroleum, but its properties remained unchanged.

Cinchonidine phenyl β -naphthyl phosphate is very readily soluble in chloroform, and dissolves freely in benzene or ethyl acetate, but is practically insoluble in ether, light petroleum, or water; it slowly decomposes at its melting point.

Cinchonine Phenyl β -Naphthyl Phosphate.

This compound was obtained by double decomposition as an oil, which solidified in the course of some hours. It separated from aqueous methyl alcohol in small needles, and was repeatedly crystallised from this solvent, but there was no sign of a resolution having occurred, and the various fractions melted practically simultaneously at 178—181°. It was also repeatedly crystallised from a mixture of benzene and light petroleum, but its melting point underwent no change.

The salt dissolves freely in alcohol, acetone, or benzene, but is practically insoluble in water or light petroleum.

Brucine Phenyl β -Naphthyl Phosphate.

The precipitated brucine salt was washed with boiling water, and kept during several days, but it did not crystallise, and separated from its solutions in aqueous alcohol or aqueous acetone as a viscid oil. It was, therefore, dried at 100°, and then dissolved in anhydrous ethyl acetate, from which it was deposited in a resinous form. When precipitated from its hot ethyl acetate solutions with light petroleum, it was obtained in a very viscous state, but at the ordinary temperature it separated in flocculent masses, which changed into a crystalline powder as the proportion of light petroleum was increased. The salt was systematically crystallised from this mixture, and was thus separated into five fractions, but so far as could be ascertained it remained unchanged. The various fractions showed the same behaviour; when placed for a few moments on porous earthenware, and then quickly transferred to capillary tubes, they began to sinter and froth from about 65°; if left in the air for a short time, they absorbed moisture, and first became sticky and then hard again; when heated slowly in a water-oven from about 50°, they first became pasty, and then gave a hard, brittle solid, but even after six hours at 100° they still retained solvent, and began to sinter and froth from about 110°; they melted immediately with effervescence when they were suddenly heated at about 160°. Attempts to obtain crystals free from solvent and having a definite melting point were unsuccessful.

The salt is readily soluble in cold alcohol, acetone, or chloroform, and also in hot benzene, but it is practically insoluble in water or light petroleum.

l-Menthylamine Phenyl β -Naphthyl Phosphate.

The oil which was precipitated from a solution of the sodium salt on the addition of excess of *l*-menthylamine hydrochloride solidified after a short time, and, after being washed with water, it crystallised from aqueous methyl alcohol in very slender needles. The crude product was recrystallised from this solvent six times, but as its melting point only rose 2° , it was concluded that a resolution had not occurred. The use of other solvents also failed to bring about any change in the properties of the salt, and its melting point remained constant at $181\text{--}182^{\circ}$. The compound is readily soluble in alcohol, acetone, or warm ethyl acetate, but it is only very sparingly soluble in boiling light petroleum, and almost insoluble in water; in aqueous alcoholic solution it is hydrolysed to some extent, and *l*-menthylamine volatilises when the solution is boiled.

Its specific rotation was determined in methyl-alcoholic solution:

0.3745, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha -0.46^{\circ}$, whence $[\alpha]_D -15.5^{\circ}$.

Resolution of Phenyl β -Naphthyl Hydrogen Phosphate.

Pure phenyl- β -naphthylphosphoryl chloride was treated with a slight excess of *l*-menthylamine in ethereal solution, and the liquid was then boiled on a reflux apparatus for some time; the precipitated *l*-menthylamine hydrochloride was collected, the ether was evaporated, and the crude oily product was repeatedly washed with a dilute solution of sodium carbonate, and finally with dilute hydrochloric acid, in order to decompose any *l*-menthylamine salt and remove its decomposition products.

The residual menthylamide was a colourless oil, readily soluble in cold light petroleum; it remained liquid for some time, and separated in an oily condition from various solvents, but from its solution in moderately concentrated aqueous acetone, crystals were slowly deposited. When repeatedly recrystallised from this solvent, these deposits ultimately yielded a well-defined substance, which melted sharply at $135\text{--}136^{\circ}$, and underwent no change when it was crystallised from other solvents.

α -Isomeride.—The pure compound, melting at $135\text{--}136^{\circ}$, is an *l*-menthylamide of phenyl β -naphthyl hydrogen phosphate:

0.1864 gave 0.4890 CO_2 and 0.1280 H_2O . $\text{C}=71.5$; $\text{H}=7.6$.

$\text{C}_{26}\text{H}_{32}\text{O}_3\text{NP}$ requires $\text{C}=71.4$; $\text{H}=7.3$ per cent.

Its specific rotation was determined in methyl-alcoholic solution:

0.584, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 1.74^\circ$, whence $[\alpha]_D - 37.2^\circ$.

This *l*-menthylamide separates from aqueous acetone, ethyl acetate, and ether in lustrous needles; it is only very sparingly soluble in boiling light petroleum (60—70°), and practically insoluble in water. It is very stable towards alkalis, and it does not undergo any appreciable decomposition when it is heated for a short time with a solution of sodium carbonate, or even sodium hydroxide.

β -Isomeride.—The more readily soluble fractions of the original *l*-menthylamide had very indefinite melting points, which ranged from about 125° down to about 75°, and the whole behaviour of the crude preparation showed clearly that it was a mixture. Those fractions which melted completely below about 100° were put together, and as they were found to contain a little *l*-menthylamine salt, they were dissolved in alcohol, the solution was treated with excess of sodium carbonate, and the liberated base was distilled in steam. The presence of this *l*-menthylamine salt was due to the fact that this salt is only very slowly and partly decomposed when it is left in contact with a cold aqueous solution of sodium carbonate; hence it was not completely removed when the crude *l*-menthylamide was purified in the manner mentioned above.

The readily soluble *l*-menthylamide was next fractionally crystallised from hot light petroleum, and the first deposit, which might have contained a considerable proportion of the sparingly soluble α -isomeride, was rejected. The mother liquors gave on evaporation an almost colourless residue, free from *l*-menthylamine salt, which melted from about 80° to 90°. This preparation was dissolved in methyl alcohol, and the solution was allowed to evaporate spontaneously; it deposited colourless rosettes of slender needles, which melted at 94—96°.

This compound is also an *l*-menthylamide of phenyl β -naphthyl hydrogen phosphate:

0.1724 gave 0.4514 CO₂ and 0.1196 H₂O. C=71.4; H=7.7.

Its specific rotation was determined in methyl-alcoholic solution with two different preparations; one of these was a portion of the sample which had been analysed:

0.5367, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 1.24^\circ$, whence $[\alpha]_D - 28.9^\circ$.

0.3043, made up to 20 c.c., gave, in a 2-dcm. tube, $\alpha - 0.89^\circ$, whence $[\alpha]_D - 29.1^\circ$.

This β -*l*-menthylamide resembles the α -isomeride very closely in all ordinary properties, and differs from it merely in being more

readily soluble; thus the β -isomeride dissolves readily in boiling light petroleum ($60-70^\circ$), whereas the α -compound dissolves in small quantities only. Like the α -compound, it is very stable towards alkalis, and when it is boiled for a short time with a solution of sodium carbonate, the odour of *l*-menthylamine is not observed; this fact rendered it an easy matter to prove that the preparation was perfectly free from *l*-menthylamine phenyl β -naphthyl phosphate.

The difference between the α - and β -isomerides, both as regards melting point and specific rotation, is considerably greater than in the case of the isomeric *l*-menthylamides of phenyl *p*-tolyl hydrogen phosphate; it may be noted also that whereas the more readily soluble *l*-menthylamide of the acid just mentioned has the higher specific rotation, it is the more sparingly soluble isomeride of phenyl β -naphthyl hydrogen phosphate which is the more optically active.

Although there can be little doubt that the isomerides described above are derived from *d*- and *l*-phenyl β -naphthyl hydrogen phosphates respectively, the acids themselves could not be obtained from their *l*-menthylamides.

Phenyl- β -naphthylphosphoramide, $\text{PO}(\text{OPh})(\text{OC}_{10}\text{H}_7) \cdot \text{NH}_2$.

Phenyl- β -naphthylphosphoryl chloride reacts readily with a moderately concentrated aqueous solution of ammonium hydroxide at the ordinary temperature, and in the course of about half an hour it is converted into a crystalline amide. The crude product melted at $150-152^\circ$, and showed the properties of a homogeneous substance; when crystallised from ethyl alcohol, its melting point rose to $152-153^\circ$, but underwent no further change when the compound was recrystallised:

0.3052 gave 12.7 c.c. N_2 at 18.5° and 768 mm. $\text{N} = 4.84$.

$\text{C}_{16}\text{H}_{14}\text{O}_3\text{NP}$ requires $\text{N} = 4.68$.

The *amide* forms lustrous plates, and is readily soluble in chloroform and moderately easily so in benzene or ethyl alcohol, but only sparingly so in ether, light petroleum, or hot water. It is very stable towards alkalis, and when it is heated with potassium hydroxide solution there is no appreciable evolution of ammonia until most of the water has boiled away and a high temperature has been reached.

Phenyl-β-naphthylphosphor-p-toluidide,
 $\text{PO}(\text{OPh})(\text{OC}_{10}\text{H}_7) \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}.$

The interaction of phenyl-β-naphthylphosphoryl chloride and *p*-toluidine (2 mols.) occurs readily in benzene solution at the ordinary temperature, but to ensure the completion of the change, the mixture was heated during about an hour. The precipitate of toluidine hydrochloride having been separated and the solution evaporated, the oily *p*-toluidide was washed with water and a little dilute aqueous alcohol; it then solidified completely, and was easily crystallised from a mixture of benzene and light petroleum. The preparation showed throughout the behaviour of a homogeneous substance, and its melting point remained unaltered after repeated crystallisation:

0·3882 gave 12·4 c.c. N_2 at 19° and 768 mm. $\text{N}=3\cdot7$.

$\text{C}_{23}\text{H}_{20}\text{O}_3\text{NP}$ requires $\text{N}=3\cdot6$ per cent.

The compound melts at $126\text{--}127^\circ$, and is readily soluble in alcohol, ether, acetone, and most other common solvents, with the exception of light petroleum and water; like the amide, it is very stable towards alkalis.

Phenylphosphordi-p-toluidide, $\text{PO}(\text{OPh})(\text{NH} \cdot \text{C}_6\text{H}_4\text{Me})_2.$

Phenylphosphoryl chloride is readily acted on by *p*-toluidine (4 mols.) in benzene solution, but the reaction is not completed until the mixture has been heated during about an hour. The precipitated toluidine hydrochloride having been separated by filtration, the benzene was distilled, and the residue repeatedly washed with warm water; the product then solidified, and when recrystallised from aqueous alcohol it showed the properties of a homogeneous substance:

0·3943 gave 27·0 c.c. N_2 at $18\cdot5^\circ$ and 767 mm. $\text{N}=7\cdot98$.

$\text{C}_{20}\text{H}_{21}\text{O}_2\text{NP}$ requires $\text{N}=7\cdot95$ per cent.

Phenylphosphordi-p-toluidide melts at $147\text{--}148^\circ$; it dissolves readily in ethyl acetate, and moderately easily in ether, chloroform, or alcohol, but only very sparingly in light petroleum.

This work was commenced in conjunction with Mr. B. D. W. Luff (1851 Exhibition scholar); Mr. Sherwood, B.Sc., and Mr. T. E. Smith, B.Sc., have also taken some part in it.—F. S. K.

UNIVERSITY COLLEGE,
 NOTTINGHAM.

LXXI. — *The Absorption Spectra of Permanganates in Certain Solvents.*

By THOMAS RALPH MERTON, B.Sc.(Oxon.).

THE absorption spectra of the permanganates have been the subject of numerous investigations; a complete bibliography of the subject will be found in Kayser's "*Handbuch der Spectroscopie*," Vol. III., p. 415 (see also p. 116). In some respects the most important work is that of Ostwald (*Zeitsch. physikal. Chem.*, 1892, 9, 579), who measured the positions of the four least refrangible absorption bands in dilute aqueous solutions of thirteen different permanganates, and found that, within the limits of experimental error, the spectra were identical. From these results he concluded that in the dilute solutions the salts were completely dissociated, and that the colour was due to the free permanganion.

The object of the present investigation has been to examine the absorption spectra of permanganates in other solvents than water, in which the dissociation of the salt into ions would be less complete. Measurements have been made of the three least refrangible bands in the spectra of potassium, calcium, barium, and zinc permanganates, in water, acetone, acetic anhydride, acetonitrile, methyl acetate, pyridine, methyl alcohol, ethyl alcohol, and ethylene glycol, except in those cases where the reaction between the salt and solvent is too rapid for trustworthy measurements to be made.

EXPERIMENTAL.

In the case of solutions of permanganates, the well-defined nature of the bands enables measurements of the points of maximum absorption to be made visually with fairly concordant results, without having recourse to photometric methods. It was found that the cross wires of the telescope could be set on the point of maximum absorption with results which did not differ by more than ± 5 Ångström unit. The instrument used was a Hilger constant deviation type spectroscope, with which wave-lengths could be read off direct on a helical drum to ± 2 or ± 3 Ångström unit. For making measurements of absorption spectra, the slit was set to a suitable breadth, and the fiducial adjustment was made by setting the cross wires (by means of a screw movement in the eyepiece) to the middle of a standard bright line, the reading on the helical drum being previously set to the corresponding wave-length; this adjustment was performed whenever it was found desirable to alter the breadth of the slit. As a source of illumination, an ordinary electric filament lamp was used, the solutions

being contained in test-tubes placed in front of the slit of the spectroscope. The mean value of five or six determinations of the maximum of each absorption band was taken, and it is probable that the mean values given are correct to ± 3 Angström unit.

All permanganates react more or less rapidly with the organic solvents investigated. Of the salts used, the zinc salt was found to be the most active. The reaction, however, takes place much less rapidly at 0° , and the solvents were therefore cooled in a vessel of crushed ice and water before the solution was made up. Owing to the rapidity of oxidation, the solutions could not be made up to any known concentration, but, on the assumption that the intensity of colour is the same in all the solvents for the same concentration, a colorimetric estimate shows that the concentrations were of the order of $0.0006-N$.

The organic solvents were obtained from Kahlbaum. The methyl and ethyl alcohols were dried by treatment with calcium turnings, the acetone and pyridine with barium oxide, and the acetonitrile with phosphoric oxide. As in many cases the presence of a small quantity of water produces a marked change in physico-chemical properties, the effect of adding a drop of water to each solution was examined. The reduction of the permanganate usually took place much more rapidly, but no change in the absorption bands could be detected, and it is therefore probable that such traces of water as might have been present in the solvents produced changes in the absorption spectra which were well within the experimental error.

The measurements of the maxima are given in Angström units in the table on p. 639.

In every case, the position of the bands in a particular solvent is the same for the four different permanganates used, showing that the influence of the cation on the absorption lies within the limits of the experimental error of the determinations, although in some of the solvents, for example, methyl acetate, dissociation must have been far from complete.

No explanation can be offered of the change of position of the bands in different solvents. Kundt's law is not in accordance with the facts, there being no apparent connexion between the optical properties of the solvents and the position of the bands, and no connection has been found between the influence of the solvents and their behaviour in other respects.

In order to investigate further the influence of the state of the salt on the nature of the absorption, the position of the bands have been measured for a solid solution of potassium permanganate in potassium perchlorate, in which dissociation can hardly be supposed

Solute.	Solvent.	Observed wave-length.		
		5719	5477	5256
Potassium permanganate	Water.....	5718	5480	5257
Calcium ".....	".....	5718	5478	5253
Barium ".....	".....	5721	5474	5255
Zinc ".....	".....	5735	5496	5276
Potassium	Acetone	5735	5493	5275
Calcium ".....	".....	5737	5492	5272
Barium ".....	".....	5737	5496	5277
Zinc ".....	".....	5720	5480	5258
Potassium	Methyl acetate ...	5719	5479	5259
Calcium ".....	".....	5720	5479	5258
Barium ".....	".....	5719	5480	5260
Potassium	Acetic anhydride	5738	5490	5271
Potassium	Pyridine.....	5734	5493	5277
Calcium ".....	".....	5735	5493	5275
Barium ".....	".....	5733	5492	5275
Zinc ".....	".....	5718	5478	5258
Potassium	Acetonitrile	5719	5477	5257
Calcium ".....	".....	5719	5477	5257
Barium ".....	".....	5719	5477	5257
Zinc ".....	".....	5721	5475	5258
Potassium	Methyl alcohol...	5747	5505	5285
Calcium ".....	".....	5746	5505	5281
Barium ".....	".....	5748	5505	5282
Zinc ".....	".....	5749	5504	5282
Potassium	".....	5747	5503	5282
Calcium ".....	Ethyl alcohol ...	5747	5503	5282
Barium ".....	".....	5746	5502	5284
Zinc ".....	".....	5747	5503	5281
Potassium	".....	5730	5484	5267
Potassium	Ethylene glycol	5747	5504	5280
	{ Ethyl and amyl } alcohols (equal volumes). }			

to occur. The general character of the spectrum is the same as in the case of a liquid solution, but the bands are shifted towards the violet end of the spectrum. The following results were obtained:

Mean wave-length: 5577, 5345, 5135.

The position of the bands in water is thus intermediate between the positions in the alcohols pyridine and acetone, and the positions in the solid solution.

It would seem, therefore, that the general nature of the absorption is due to the atomic grouping MnO_4 , and that it is influenced very little, if at all, by the nature of the cation or the extent of dissociation, the position of the points of maximum absorption being determined by the nature of the medium in which the salt is dissolved.

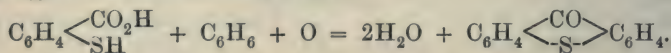
* I should like to express my thanks to Professor Jackson, of King's College, London, to Mr. H. B. Hartley, of Balliol College, and to Mr. D. H. Nagel, of Trinity College, Oxford, for their valuable advice in this investigation.

18, GROSVENOR STREET,
LONDON, W.

LXXII.—*The Interaction of Aromatic Disulphides and Sulphuric Acid.*

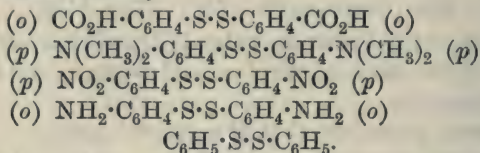
By WILLIAM GEORGE PRESCOTT and SAMUEL SMILES.

THE experiments described in this paper are an extension of those previously carried out (Davis and Smiles, *Trans.*, 1910, **97**, 1290) on the synthesis of thioxanthenes from thiosalicylic acid and aromatic compounds. It was then shown that the thioxanthenes are formed from these reagents in the presence of sulphuric acid, the hydrogen of the thiol group and aromatic nucleus being removed by oxygen from the mineral acid:



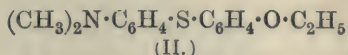
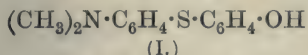
In explaining this somewhat remarkable reaction, cogent reasons were given for rejecting the supposition that these hydrogen atoms are directly removed by simultaneous oxidation. It was further shown that the only rational interpretation is afforded by the hypothesis that the thiol group is first oxidised to the sulphylic arrangement, which then condenses with the aromatic nucleus, water being eliminated.

Since Stenhouse (*Annalen*, 1869, **149**, 250) has shown that the mercaptans are oxidised by sulphuric acid to the disulphides, it appeared probable that these might play an accompanying rôle in the synthesis of thioxanthone. We have therefore examined the behaviour of aromatic disulphides with sulphuric acid. Five cases have been studied, namely:



It has been found that in sulphuric acid certain of these substances readily react with simple aromatic derivatives, sulphurous acid being continuously evolved. The products of the reaction have been found to be derivatives of unsymmetrical monosulphides, in which one aryl group is that of the original disulphide, the other being provided by the aromatic compound chosen as the reagent. Thus, with benzene, di-*o*-thiobenzoic acid yields thioxanthone; with toluene, methylthioxanthone; with anisole, methoxythioxanthone; and so on. It is clear that these substances are produced from the *o*-carboxysulphides by the dehydrating influence of the mineral acid (see Graebe, *Annalen*, 1891, **263**, 1).

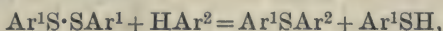
With phenol, di-*p*-thiodimethylaniline yields hydroxydimethylaminophenyl sulphide (I), and with phenetole the corresponding ethoxy-derivative (II):



but both of these finally appear as sulphonic derivatives, which have been isolated as sodium or ammonium salts.

This reaction, however, is not universal, for di-*p*-nitrophenyl-disulphide and di-*o*-thioaniline appear to be inactive. In the former case this is not surprising, for many of the reactions of sulphur in aromatic compounds appear to be inhibited by the presence of nitro-groups; but with the latter substance we are entirely unable to account for the inactivity. Diphenyl disulphide readily undergoes this reaction, but the products with phenol and phenetole are not crystalline, and are so difficult to purify that we have not been able to obtain them in a condition suitable for analysis.

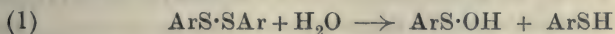
Returning to the carboxy- and dimethylamino-disulphides, it might be supposed that with these the reaction should be expressed in general terms as follows:



the mercaptan being oxidised by the sulphuric acid to disulphide, which is then ready to continue this change with excess of the aromatic derivative.

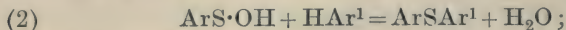
It is evident, however, that this does not express the true state of affairs, for diphenyl disulphide and its carboxy- or dimethylamino-derivatives may be treated with boiling phenol or phenetole without decomposition. Further consideration shows that rupture of the dithio-system may be effected with sulphuric acid alone; thus, diphenyl disulphide and this acid interact at about 20—30°, giving the thianthrens (Fries and Volk, *Ber.*, 1909, **42**, 1170). The two latter-named disulphides are not so readily attacked, but interaction begins at about 100°, with evolution of sulphurous acid.

It therefore appears that a preliminary fission of the disulphide is effected by the mineral acid, and at least one of the products, which with some disulphides may be present only in small amount, must be capable of reacting with the aromatic compound, forming the unsymmetrical sulphide. Accordingly there is no satisfactory alternative to the hypothesis that these disulphides are broken by the sulphuric acid:



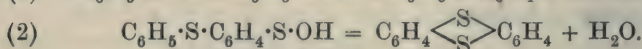
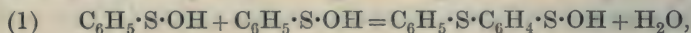
into mercaptan and the sulphylic acid. For reasons which have been elsewhere given (Davis and Smiles, *Trans.*, 1910, **97**, 1290),

it is permissible to assume that the latter substance is capable of condensing with the aromatic compound introduced:

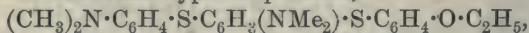


whilst it is certain (Stenhouse, *loc. cit.*) that the remaining mercaptan must be re-oxidised by the sulphuric acid to the original disulphide. Thus sulphurous acid is continually liberated during the reaction, and rupture of the disulphide continues until all has been converted into monosulphide.

In the want of any method of isolating these unstable sulphonylic acids, no more severe test of this hypothesis can be devised than to examine its fitness to account for certain abnormal reactions of disulphides. It has been observed (Fries and Volk, *Ber.*, 1909, **42**, 1170) that diphenyl and other disulphides, when heated alone in sulphuric acid, react vigorously, producing thianthrens. According to the present hypothesis, it is evident that no other aromatic compound being now available, the sulphonylic acid condenses with itself or the mercaptan, forming the unsymmetrical sulphide (1):



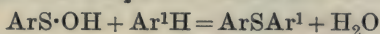
which finally yields the thianthren by intramolecular condensation. The foregoing interpretation of this reaction is certainly simpler than that put forward by Fries and Volk (*loc. cit.*), who have assumed disulphoxides, thianthren oxides, and other substances to be formed as intermediate products. We do not, however, suggest that this is the sole reaction which may take place when a disulphide is heated with sulphuric acid, for, with substances of the high reactivity which must be ascribed to the sulphonylic acids, the decomposition must be various. In the experimental part of this paper another abnormal type of product,



is described; it is obtained from the interaction of phenol with di-*p*-dimethylaniline disulphide, and its formation is fully explained by this hypothesis (see p. 648).

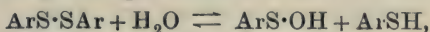
It is necessary further to discuss the nature of the decomposition of the disulphides. With the carboxy- and dimethylamino-disulphides the reaction does not proceed to any appreciable extent with cold sulphuric acid alone, for these may be almost entirely recovered unchanged after solution in that medium; in fact, under these conditions it is only when the simpler aromatic derivative is present that any clear evidence of the decomposition can be detected. On the addition of this aromatic compound to the mixture of disulphide and sulphuric acid, the evolution of sulphurous acid immediately

begins, and this is renewed with each fresh addition until excess has been introduced. If the reacting mixture is examined at an intermediate stage, a mixture of disulphide and monosulphide is found. According to the present hypothesis, which is summed up as follows:



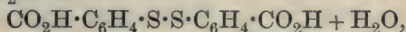
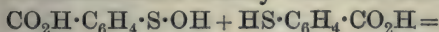
it is seen that the sulphonylic acid as soon as it is formed is removed by the aromatic derivative, being then converted into the stable monosulphide, and the remaining mercaptan is re-oxidised (Stenhouse, *loc. cit.*) by the sulphuric acid to the disulphide, which is then available for renewed interaction.

The fact that decomposition cannot be detected in appreciable amount unless the sulphonylic acid is removed in this manner, strongly suggests that the law of mass action plays a part in this reaction, the change being a reversible one:

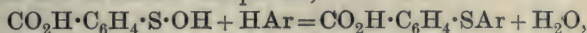


and that in sulphuric acid the reaction from right to left in the above equation has very much the greater velocity, although this may vary with different disulphides. This conception offers a facile explanation of the reaction of Stenhouse, where the disulphides are thus seen to be formed by condensation of excess of mercaptan with the sulphonylic acid which results from preliminary oxidation (see also Davis and Smiles, *loc. cit.*). The discussion of the conditions under which the sulphonylic acids are produced from the mercaptans would lead beyond the present question, and it is therefore postponed.

Turning finally to the bearing which these experiments have on the synthesis of thioxanthone from *o*-thiolbenzoic acid, it is seen that no conclusive answer can be given to the question whether di-*o*-thiobenzoic acid there occurs as an intermediate product. The matter seems ultimately to depend on whether the sulphonylic acid condenses more readily with the excess of mercaptan,



than with the aromatic compound,



but at present there are no means of determining the relative speeds of these reactions. It is highly probable that some dithio-acid does occur during the interaction, but its formation is not necessary.

In conclusion, it may be remarked that there are many other substances containing bi- and quadri-valent sulphur the complex reactions of which have been explained by assuming the formation of a sulphonylic acid at some stage or other in their decomposition.

Although it seems to us that in some of these cases the evidence is not sufficiently strong to establish firmly this assumption, we consider that in the present instance it is fully justified, and we are unable to discover any satisfactory alternative. The advantage of the hypothesis is further apparent in the simple manner with which it correlates all the known reactions of aromatic mercaptans and disulphides in sulphuric acid.

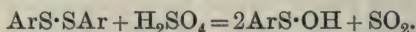
The results of this discussion are summed up as follows:

(1) From the formation of unsymmetrical monosulphides by interaction of an aromatic compound, sulphuric acid, and *o*-dithiobenzoic acid, or *p*-dithiodimethylaniline, it is concluded that the latter substances are decomposed by the mineral acid into mercaptan and sulphylic acid.

(2) The general character of this reaction indicates that it is reversible.

(3) The hypothesis advanced correlates all the known reactions of disulphides and mercaptans in sulphuric acid solution: formation of disulphides from mercaptans, of thianthrens from disulphides, and of unsymmetrical monosulphides from disulphides and aromatic compounds.

(4) The net result of the interaction of sulphuric acid with these disulphides in presence of an aromatic compound may be represented as follows:



EXPERIMENTAL.

Di-o-thiobenzoic Acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$.

The acid employed in these experiments was prepared by direct oxidation of *o*-thiolbenzoic acid. The process was as follows. Twenty grams of the latter substance were dissolved in about 150 c.c. of alcohol, to which a few c.c. of concentrated hydrochloric acid had been added. Twenty-five grams of ferric chloride were added to the mixture, which was then heated for about an hour on the water-bath. When the reacting mixture was cooled, a small quantity of di-*o*-thiobenzoic acid separated, but the bulk of the product was obtained by the addition of water. The yield of the required acid was almost theoretical. After recrystallisation from alcohol, the product melted at 287—288° (Gattermann, *Ber.*, 1899, **32**, 1150, gives 289°, and Jones, *Amer. Chem. J.*, 1895, **16**, 366, gives 288—290°).

Interaction with Toluene and Sulphuric Acid.

Fourteen grams of di-*o*-thiobenzoic acid were suspended in 100 c.c. of concentrated sulphuric acid; excess of toluene was then added to

the mixture, which was violently shaken in order to form an emulsion. Interaction, accompanied by evolution of sulphurous acid, set in immediately, and the reacting mixture was set aside for fifteen hours. It was then heated on the water-bath for two hours, toluene being continually added with renewed shaking during this process. The orange solution was finally poured on crushed ice. After the lapse of twenty-four hours, the solid material was collected, washed with water, and then triturated with aqueous alkali hydroxide in order to remove the unchanged acid. The residue was again collected, purified by thorough washing with water, and then dried by fusion in the steam-oven. The product was finally purified by distillation in small quantities under atmospheric pressure. It melted at 96—97°, whether alone or mixed with a sample of methylthioxanthone from other sources, and showed all other properties elsewhere attributed (Davis and Smiles, *Trans.*, 1910, **97**, 1290) to that substance. (Found, C=74·6; H=3·7. Calc., C=74·3; H=4·4 per cent.) The yield was 10 grams, or 50 per cent. of the theoretical.

Interaction with Benzene and Sulphuric Acid.

Ten grams of the di-*o*-thiobenzoic acid were treated with benzene in a manner similar to that described in the preparation of methylthioxanthone.

The properties of the product, melting point (208°), fluorescence, and so on, were found to be identical with those assigned to thioxanthone prepared by other methods. The melting point of the product was unaltered by admixture with a sample of thioxanthone. The yield of thioxanthone was nine grams, or about twenty-five per cent. of the theoretical.

Interaction with Anisole and Sulphuric Acid.

The general outlines of the process adopted were again similar to those adopted in the preparation of methylthioxanthone; the sole difference being that during the interaction, anisole was added continually, and in large excess, in order to overcome the loss of this substance by sulphonation. After recrystallisation from acetic acid, the product was obtained in bright yellow needles, which melted at 128°, whether heated alone or with a sample of methoxythioxanthone from other sources (m. p. 128—129°). It also showed the characteristic fluorescence of the thioxanthenes in sulphuric acid or glacial acetic acid.

Di-p-thiodimethylaniline, $(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2$.

This disulphide was prepared by the interaction of dimethylaniline and sulphur monochloride (Merz and Weith, *Ber.*, 1886, **19**, 1371). The orientation of the dithio- and dimethylamino-groups in this substance has recently been proved by Fichter and Tamm (*Ber.*, 1910, **43**, 3038).

Interaction with Phenetole and Sulphuric Acid.

The disulphide, in quantities of about five grams at a time, was dissolved in 50 c.c. of concentrated sulphuric acid. When phenetole was added to the mixture, evolution of sulphurous acid immediately took place, and this continued when the addition was repeated at intervals during one hour at the atmospheric temperature and a further half-hour on the water-bath. The addition of phenetole was regulated so that the mixture retained a clear orange colour; when a blue colour appeared this was immediately discharged by excess of the reagent. The completion of the reaction is indicated by the stability of the orange tint; when this no longer changed to blue on setting the mixture aside for ten minutes or so, the solution was poured on crushed ice and rendered alkaline with aqueous ammonia. After the lapse of twenty-four hours, the product had separated as a semi-solid mass; this was collected and extracted with chloroform. The portion which was insoluble in this medium was crystalline, and it was purified by recrystallisation from hot water.

Further investigation showed that the substance was an ammonium salt of a sulphonic acid containing water of crystallisation:

0.1306 gave 0.2382 CO_2 and 0.0758 H_2O . $\text{C}=49.77$; $\text{H}=6.46$.

0.1020 „ 0.1268 BaSO_4 . $\text{S}=17.1$.

0.3130 „ 20.5 c.c. N_2 at 17° and 776 mm. $\text{N}=7.7$.

0.5040 lost 0.0226 H_2O at 100° . $\text{H}_2\text{O}=4.4$.

$\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_2\text{S}_2\cdot\text{H}_2\text{O}$ requires $\text{C}=49.49$; $\text{H}=6.19$; $\text{S}=16.5$;
 $\text{N}=7.22$; $\text{H}_2\text{O}=4.64$ per cent.

The ammonium sulphonate of ethoxydimethylaminophenyl sulphide forms colourless prisms, which are sparingly soluble in cold water. When boiled with aqueous sodium hydroxide, it yields ammonia, and on cooling the solution the sodium salt is precipitated in needles. The aqueous solution when acidified with hydrochloric acid yields, on addition of chloroplatinic acid, a sparingly soluble platinichloride, but this appears to be unstable in the dry condition. The solution of this ammonium salt in dilute sulphuric acid assumes

a deep blue colour when a few drops of dichromate solution are added. The same colour change is effected by warm concentrated sulphuric acid.

The portion of the product which is soluble in chloroform consists of an oily base, or probably a mixture of bases; this was not further investigated on account of its uninviting physical properties and the difficulty of obtaining definite derivatives. There is little doubt, however, that the chief constituent is a base similar to that isolated from phenol and the disulphide.

The yield of ammonium salt obtained by this process varies considerably, and at best it is not good. It is important to notice that phenetole should always be present in excess during the reaction, and this is best attained by working with very small quantities of disulphide and reducing the amount of sulphuric acid.

Interaction with Phenol and Sulphuric Acid.

The process followed in this reaction, and the observations to be made in order to obtain maximum yields of the desired products, are the same as described in the foregoing paragraphs. The acid solution obtained by pouring the reacting mixture on ice is neutralised with sodium carbonate, and the solution, together with the insoluble products, are extracted with chloroform. The portion of the precipitated material which is insoluble in that medium was found to be the *sodium sulphonate of hydroxydimethylaminophenyl sulphide*. It was recrystallised from water, but it is difficult to obtain in the pure condition on account of its high solubility in that medium:

0.1020 gave 0.1436 BaSO_4 . $\text{S}=19.3$.

0.6032 „ 22.0 c.c. N_2 at 14° and 776 mm. $\text{N}=4.3$.

0.3148 „ 0.061 Na_2SO_4 . $\text{Na}=6.3$.

$\text{C}_{14}\text{H}_{14}\text{O}_4\text{NS}_2\text{Na}$ requires $\text{S}=18.6$; $\text{N}=4.0$; $\text{Na}=6.6$ per cent.

The substance occurs in nodular aggregates of fine needles. A deep blue colour is imparted to acidified aqueous solutions by the addition of a few drops of aqueous alkali hydroxide.

The portion which was soluble in chloroform was treated as follows. The solvent was evaporated, and the residue was treated with concentrated hydrochloric acid. The solid hydrochloride which separated was collected, washed with aqueous hydrogen chloride, and finally decomposed with aqueous alkali hydroxide. The base which separated was removed by shaking with benzene. This treatment removed the soluble crystalline base, leaving a colloidal base suspended in the liquid. Evaporation of the benzene yielded a colourless, crystalline residue, which was further purified with alcohol. Several specimens were analysed:

0.1052 gave 0.2571 CO_2 and 0.0560 H_2O . $\text{C} = 66.6$; $\text{H} = 5.9$.

0.1026 „ 0.2497 CO_2 and 0.0562 H_2O . $\text{C} = 66.3$; $\text{H} = 6.0$.

0.1082 „ 0.1232 BaSO_4 . $\text{S} = 15.6$.

$\text{C}_{22}\text{H}_{24}\text{ON}_2\text{S}_2$ requires $\text{C} = 66.6$; $\text{H} = 6.0$; $\text{S} = 16.1$ per cent.

The substance forms colourless, feathery needles, which melt somewhat indefinitely in the neighbourhood of 125° . It is readily soluble in dilute acids, and with concentrated aqueous alkali hydroxide it furnishes an unstable *sodium* salt, which separates from the mother liquor in colourless plates. This salt is decomposed by water.

According to the analytical data and properties, this substance must contain two thiodimethylaniline residues, $\text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2$ united with one hydroxyphenyl group. Since the compound is not altered by reducing agents, it follows that the former groups do not occur as a dithio-arrangement; hence, the only structure for this substance which satisfies the conditions is one where the sulphur is attached to the aromatic nuclei, as:

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_3(\text{NMe}_2) \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ or

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2$,

whence it is seen to be the *thiodimethylanilino*-derivative of *hydroxydimethylaminophenyl sulphide*.

The formation of this substance is fully explained by the hypothesis developed in the theoretical part of this paper; for it is evident that, if at any period during the preparation excess of phenol is not present, the sulphylic acid, $(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{OH}$, may condense with unsymmetrical sulphide already formed. The yield of this substance is in most cases extremely small.

Unfortunately, we have not been able to define the exact conditions necessary for the maximum yield, and thus a sufficient quantity for the preparation of derivatives and determinations of molecular weight has not been available. Attempts to obtain it in larger quantity by conducting the preparation so that a large excess of phenol is avoided have always yielded a large amount of the colloidal insoluble bases, which undoubtedly are of high molecular weight. It is evident that these substances probably contain an indefinite chain of thiodimethylanilino-residues. However, the analytical data are sufficient to show that only two of these are present in the substance now described.

The interaction of di-*p*-nitrophenyl sulphide and of di-*o*-amino-phenyl sulphide with phenetole was investigated by heating these substances in concentrated sulphuric acid. Only slight reaction could be detected at 100° by the evolution of sulphurous acid, but the original disulphides were recovered from the reacting mixtures and identified by mixed melting points. With diphenyl disulphide

and phenol or phenetole the products were colloidal, and did not invite further examination.

The interaction of disulphides with aluminium chloride and similar substances is now being investigated.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Society for a grant which has defrayed the cost of these experiments. We also wish to thank Dr. Lewis for his criticism of the theoretical part of this paper.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

LXXIII.—*The Volatile Constituents of Coal. Part II.*

By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

DURING the past three years the Mining Association of Great Britain has been engaged in an inquiry into the nature of coal dust explosions and the means of preventing them. A particular branch of the inquiry deals with the influence of the chemical composition of coal dust on its inflammability. The results obtained in the course of this investigation lead to conclusions of such a nature as to render it necessary to lay them before the Society prior to applying them to the technical problem for the elucidation of which the experiments were devised. For the experimental detail and the deductions drawn on chemical grounds, the relation of which is necessary to the formulation of our conclusions, are out of place in a technical paper, which requires to treat only of the practical application of the facts discovered, and not of the manner in which those facts have been established.

Our thanks are due to the Coal Dust Committee appointed by the Mining Association for permission to publish in this manner.

In a previous paper we have shown that the composition of the gases arising from the destructive distillation of coal undergoes a marked change at a temperature (the same for all the samples of coal tested) lying between 750° and 800° ; and that there is every evidence of a critical period in the decomposition of coal between those temperatures.

The wide differences in composition, coupled with the fact that the rate at which gas is evolved when a high temperature of distilla-

tion is employed, falls off rapidly after the first few minutes of heating, suggested that it would be profitable to examine the composition of the gases evolved during successive stages of distillation at a uniform temperature. It appeared probable that in this manner the existence of compounds of different degrees of stability under the action of heat could be recognised, and a further insight into the composition of coal thereby gained.

In the manufacture of lighting-gas it is a matter of common observation that the gas produced during the second and third half-hours from the time of charging is the richest; that is to say, has the highest "illuminating power." That produced during the next two hours is considerably poorer, whilst from then to the end of the distillation it is poorer still. Thus, W. J. A. Butterfield, in his book, *The Chemistry of Gas Manufacture*, says on page 136:

"In the manufacture of coal gas from ordinary good gas coal, when about 11,000 cubic feet of gas, having an average 'illuminating power' of about 14 standard candles when the gas is consumed at the rate of 5 cubic feet per hour in the London Argand burner, is made, the fraction produced during the first half-hour, amounting to about a seventh of the total volume, will be only about 10 candle gas. During the next hour and a-half the candle-power of the gas will be 17 to 18, and the production nearly one-half the total. During the next hour the make will be nearly a fifth of the total, but the candle-power only about 14. The remainder of the gas will be only 8 to 10 candle. These figures are, of course, only rough approximations. . . ."

It would also appear, therefore, that the greatest rate of evolution of gas corresponds with the greatest illuminating power. The exact relation that exists between the illuminating power of the gas and its composition is not known, but it can be definitely stated that a gas rich in hydrogen, at the expense of hydrocarbons, is of relatively low candle-power.

Several analyses have been published showing the variation in composition of coal gas during successive stages of its manufacture on a commercial scale, all of which point to a progressive increase in the percentage of hydrogen as distillation proceeds. The following are taken from Roscoe and Schorlemmer's *Treatise on Chemistry* (Vol. I, page 785). The samples were aspirated from the ascension pipe during the manufacture of gas from a Derbyshire gas coal, and were washed with dilute sulphuric acid to remove tarry matters and ammonia before being analysed; the temperature of the retort was about 950°.

Hours after beginning...	$\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$	$3\frac{1}{2}$	5
Hydrogen sulphide	3.8	3.1	2.8	2.1	1.2
Carbon dioxide	3.0	2.8	2.6	2.3	1.7
Unsaturated hydrocarbons	8.65	5.2	3.6	2.4	nil
Oxygen	nil	nil	nil	nil	trace
Carbon monoxide	4.35	5.0	4.9	4.5	3.8
Hydrogen	29.8	37.5	42.2	46.2	60.8
Saturated Hydrocarbons.....	49.7	42.05	39.4	37.5	26.3
Nitrogen (by difference)	0.7	4.35	4.5	5.0	6.2

It is, however, impossible from such analyses to differentiate entirely between the influence of time and of temperature; for the large charge of coal suddenly introduced into the hot retort is not immediately heated throughout its mass, and it may be several hours before the centre of the charge has acquired the temperature of the retort; whilst in the meantime the coal in actual contact with the hot walls will have yielded practically all its gas.

By means of an apparatus described later, we have been able to collect separately the whole of the gases evolved from different samples of coal at different stages in the heating, from the beginning of evolution of gas until its cessation. And we are satisfied that in our experiments no great interval of time elapses before the whole of the "charge" of coal employed has attained the experimental temperature.

We have already shown that a compound exists in coal which decomposes rapidly at a temperature lying between 700° and 800° , and yields hydrogen as its principal gaseous product. At the same time, it is evident that at low temperatures of distillation the paraffin hydrocarbons, and not hydrogen, are the chief products; and it seems reasonable to suppose (assuming the same compound to be responsible), that the difference is due principally to the temperature at which decomposition is effected.

From the results given in the present paper, it is apparent that coal also contains a compound of less stability to the action of heat, which yields the paraffins as its gaseous decomposition products.

Thus we find that of the first gases evolved, at temperatures either above or below the "critical period" of decomposition, the paraffin hydrocarbons form by far the largest proportions. At temperatures below the critical period, one or two per cent. of hydrogen, at most, is evolved during the first few seconds of heating.

Presumably, therefore, coal contains two types of compounds of different degrees of ease of decomposition; the one, the more unstable, yielding the paraffin hydrocarbons and no hydrogen; the other, decomposed with greater difficulty, yielding hydrogen alone

(or, possibly, hydrogen and the oxides of carbon) as its gaseous decomposition product.

"Fractional" distillation of coal in a vacuum confirms this view. It is possible by prolonged exhaustion at a low temperature to remove entirely the paraffin-yielding constituents, and leave behind a compound which decomposes at a higher temperature, and yields hydrogen. Thus a bituminous coal (coal C of our previous paper) evolved on exhaustion at 400° 25.5 c.c. of gas containing 9.4 per cent. of hydrogen and 55.0 per cent. of paraffin hydrocarbons. At 650° 96.75 c.c. of gas were evolved, containing 83.4 per cent. of hydrogen and only 1.65 per cent. of paraffins.

It appears very probable that the difference between one coal and another is determined mainly by the proportion in which these two types of compound exist, anthracite, for example, containing but little of the more unstable constituents; and that the true "coal substance," apart from the traces of sulphur compounds and other material that mask its character, is compounded of the two types which behave so differently under the action of heat.

It is for this reason that, in recording the data obtained, we have omitted any special reference to the variations in the quantities of ammonia, benzene, and unsaturated hydrocarbons that are evolved; for we do not consider that the compounds from which they are derived can rightly be regarded as entering into the composition of "coal" in the same manner as the compounds that yield the paraffins and hydrogen. It is, however, interesting to note the rapidity with which benzene and the ethylene hydrocarbons disappear from the products at high temperatures as distillation proceeds, for it is usually considered that the luminosity of coal gas is chiefly determined by their presence (see Fig. 3).

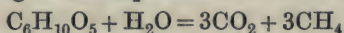
On the other hand, it is necessary to explain the variation that occurs in the quantity of carbon monoxide evolved, since it presumably arises from the decomposition or the interaction of oxygenated compounds in the coal.

From the results given in our previous paper it will be observed that the quantity of carbon monoxide evolved increases with the temperature of distillation employed. On the other hand, the percentage present in the gases, but not the actual quantity evolved, increases in a very marked manner towards the end of distillation at a uniform temperature. That is to say, the rate of formation of carbon monoxide is uniform throughout distillation at any one temperature and is maintained, whilst the rate of evolution of the other gases falls off, but increases with increased temperature.

From this we conclude that the presence of carbon monoxide in the gases is due mainly to the interaction of oxygenated compounds

with the carbon of the coal, not to direct evolution owing to the decomposition of such compounds. It most probably arises through the elimination of water from hydroxy-compounds, and the subsequent reaction of the steam thus formed with the carbon.

Considering its undoubted vegetable origin, it is natural to suppose that cellulose derivatives must enter largely into the composition of coal. The precise form that these "degradation products" take must, at present, be as much a matter of conjecture as is the manner in which they have arisen. There seems, however, to be strong presumptive evidence that micro-organisms have played an important part in the "decay" of the plant structures. The extreme resolution of cellulose by the action of *amylobacterium* takes place according to the equation:



(Hoppe-Seyler, *Zeitsch. Biol.*, 1881, **10**, 401; see also *Cellulose*, by Cross and Bevan, London, 1903), a similar decomposition being effected by the ferments present in the mud of cesspools (Hoppe-Seyler, *Ber.*, 1883, **16**, 122). Carbon dioxide and methane are, of course, the two gases most commonly met with in coal measures, and often issue in large quantities from the strata.

In addition, however, to the tendency to complete resolution as represented in the above equation, there is a tendency, as Cross and Bevan have shown (*loc. cit.*, pp. 66 and 238), towards a condensation of the carbon nuclei to still more complicated forms, accompanied by the elimination of water. This is illustrated by the following analyses given by W. A. Miller (*Organic Chemistry*, 1869, pp. 139—146) of different products of decomposition of plant tissue: *

	Humus								
	Oak	Decayed	from	Peat,	Lignite,	Coal,	Coal,	Coal,	Coal,
	wood.	oak	decayed	Dart-	Bovey.	Scotch.	Wigan	New-	Anthra-
		wood.	oak.	moor.			Cannel.	castle.	cite.
C ...	50.20	53.50	56.0	59.73	67.85	78.46	82.29	87.97	91.87
H ...	6.08	5.16	4.9	5.91	5.76	8.11	5.68	5.31	3.33
O ...	43.74	41.34	39.1	31.82	23.39	13.73	{ 8.31 }	6.72	{ 3.01 }
N ...	—	—	—	2.54	0.58				
							{ 2.18 }		{ 0.84 }

It will be seen that the carbon gradually accumulates at the expense of hydrogen and oxygen, the approximate formulæ for oak wood and for anthracite being $\text{C}_{34}\text{H}_{48}\text{O}_{22}$ and $\text{C}_{40}\text{H}_{16}\text{O}$ respectively.

There seems, therefore, to be considerable justification in assuming that one type of compound in coal, and the most important

* In quoting this series of analyses illustrating the degradation of cellulose, we do not wish to imply that we consider all anthracite coal as being formed by the prolonged duration of the agencies that have produced "bituminous" coal. On the contrary, we incline to the belief that true anthracite is derived from a different type of plant life, although doubtless by similar agencies.

type, is a degradation product of cellulose. This type, from preliminary experiments we have made on the destructive distillation at high temperatures of pure cellulose and oxycellulose, we identify with the "hydrogen-yielding constituents" indicated by our experiments with coal. The "paraffin-yielding constituents" are most probably derived from the resins and gums originally contained in the sap of the coal plants, and form the "cement" of a conglomerate, of which the cellulose derivatives are the base.

This view receives considerable support from the discovery by P. P. Bedson (*J. Soc. Chem. Ind.*, 1908, **27**, 147) that pyridine has a remarkable solvent action on part of the coal substance.

By extracting the finely divided coal (sieved through a 240-mesh sieve) in a Soxhlet apparatus with pyridine, we have obtained as much as 30 per cent. of extract of a dark chocolate-brown colour in the case of Coal A, the residue being a black, porous, coke-like mass. The destructive distillation of this residue at 900° yields as gases mainly hydrogen, carbon monoxide, and carbon dioxide—as does pure cellulose.* The extract yields a mixture of the paraffin hydrocarbons and hydrogen, the percentage of hydrogen increasing with the temperature of distillation employed.

We hope, in a future communication, to be able to give the results of a further examination of these two distinct substances into which "coal" can be mechanically separated, comparing the results of their destructive distillation, as regards both liquid and gaseous products, with those of the action of heat on cellulose and its derivatives. In the meantime we hesitate to identify absolutely the "paraffin-yielding constituent" of coal with that portion extractable by pyridine, although the results we have obtained so far are in the main favourable to such a view.

EXPERIMENTAL.

The samples of coal used were obtained in the same manner as described in our previous paper. The experiments recorded have been conducted with the samples designated A, D, and B in that paper, as being characteristic of bituminous, semi-bituminous, and anthracite coals.

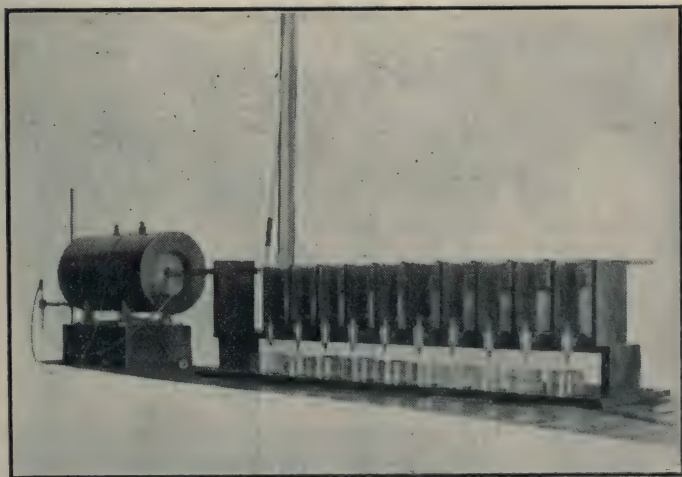
The distillation apparatus employed consisted of a platinum retort, boat, and tar-scrubber similar to that previously described, the source of heat being an electric resistance tube furnace of uniform temperature throughout its effective length.

* At a temperature of 300—400° the gases evolved on destructive distillation of pure cellulose consist almost entirely of carbon dioxide and monoxide (Chorley and Ramsay, *J. Soc. Chem. Ind.*, 1892, **11**, 872). At temperatures above 800°, however, hydrogen makes its appearance.

The main feature of the apparatus for collecting the gases (Fig. 1) is a series of ten small gas-holders (of 100 c.c. capacity) connected together by three-way T-taps. These taps are arranged so that it is a simple matter to turn the stream of gas into one gas-holder after another at a definite time. Two of the gas-holders are shown diagrammatically in Fig. 2, from which it will be seen that, with the taps in the positions numbered 1A and 2A, any gas-stream will pass into gas-holder No. 1; whilst as soon as tap No. 1 is turned into position B, gas-holder No. 1 is shut off, and the gases pass at once into gas-holder No. 2.

The gas-holder and all connexions up to the straight tap *T*

FIG. 1.



General arrangement of apparatus.

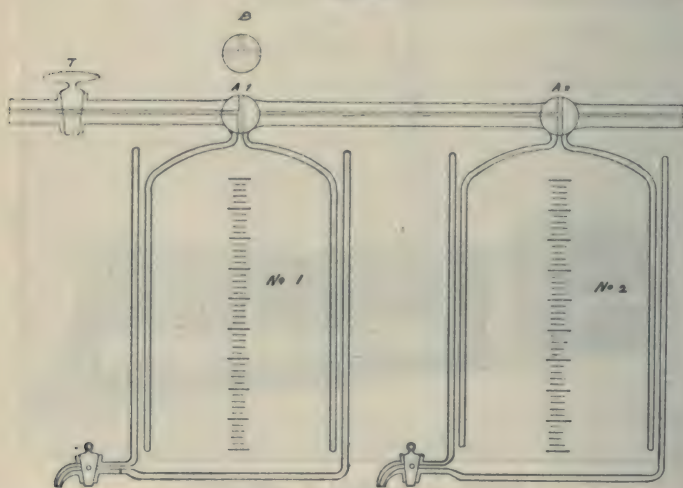
(Fig. 2), which is closed before the experiment, are filled with a mixture of equal parts of glycerol and water.

The method of conducting a distillation is as follows. Two grams of the dried and sieved coal (through a 240-mesh sieve) are mixed with three grams of ignited sand, and placed in the platinum boat. This is then put into the retort, the tar-scrubber is placed in position, and the gun-metal joint is made between the retort and the sampling apparatus. All the taps on the gas-holders are turned into the positions 1A, 2A, 3A, etc., and the retort exhausted of air through the side-tap *S* (Fig. 2). The retort is then pushed into the electric furnace, which has previously been raised to the required temperature. As soon as the pressure of the gas evolved becomes equal to the atmospheric pressure, tap *T* is opened, and the gas

passes into gas-holder No. 1; it is collected for a given time, and then passed into gas-holder No. 2, and so on.

Before starting an experiment, the temperature of the electric furnace is raised about 80° above the required distillation temperature, so as to compensate for the cooling produced by the sudden introduction of the retort, regulation being afterwards effected by means of an external resistance. As previously noted (Trans, 1910, 97, 1924), the distillation temperatures recorded are the retort temperatures, not those existing in the coal. The temperature in the coal itself reaches the retort temperature at the end of two minutes. Collection of the gases is begun one minute after the introduction of the retort in the experiments at temperatures above

FIG. 2.



Arrangement of gas-holders for collecting samples during successive intervals of time.

700° , and two minutes after, when the distillation is conducted below that temperature. In the former case, therefore, the temperature in the coal is about 30° lower than that of the retort during the first minute; in the latter case the coal has had time to attain the retort temperature before collection of the gases is begun.

A second method of distillation that we have adopted, the results obtained by which confirm our conclusions regarding the existence of two types of compounds of different degrees of stability under the action of heat, is that of fractional distillation in a vacuum. Two grams of the dried and sieved coal are mixed with 3 grams of ignited sand, and introduced into a bulb-tube of Jena glass. The

bulb is of 16 mm. internal diameter and 12 cm. long, and the neck 7.5 mm. in diameter and 19 cm. long. The mixture of coal and sand lies evenly along the bottom of the bulb, and occupies about half its volume. The neck is packed with ignited asbestos for a distance of 4 cm., and the end is attached, by means of stout rubber pressure tubing, to an automatic Sprengel mercury pump. The apparatus having been thoroughly exhausted when cold, the bulb is heated in an electric resistance tube furnace to 350°, at which temperature it is maintained for twenty-four hours, exhaustion and collection of gas being conducted continuously. The temperature is afterwards raised, by stages of 50°, to 650° (the limit imposed by the softening point of Jena glass), each successive temperature being maintained during twenty-four hours, and exhaustion being continued throughout.

Coal A (Bituminous).

Distillation at 625°:

The gases were collected during ten periods of 5 seconds each. About 2.5 c.c. were evolved during each period. The gas analyses were as follow:

TABLE I.

Percentage Composition of Gas Evolved during Different Time-intervals at 625°.

Calculated as "nitrogen-free" gas.

Period No.	(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).
NH ₃	1.00	4.35	5.50	3.80	4.50	3.35	5.20	3.45	3.75	2.75
C ₆ H ₆ ...	9.25	11.00	8.90	9.45	8.15	7.60	7.65	8.35	6.60	7.55
CO ₂	4.65	2.15	2.15	2.90	2.45	2.15	1.95	3.05	2.65	0.40
C ₂ H ₂	0.25	1.55	1.15	0.70	2.15	0.60	1.00	0.20	0.05	0.85
C ₂ H ₄ ...	2.65	2.25	3.85	3.35	2.30	3.00	1.55	1.35	2.50	1.05
CO	8.80	9.45	7.95	8.40	8.50	8.45	6.80	7.45	7.15	9.25
H ₂	3.60	2.15	2.30	3.35	2.80	3.45	2.60	1.40	1.75	nil
CH ₄	42.90	39.05	44.15	43.10	47.60	52.35	56.00	57.35	62.05	61.85
C ₂ H ₆ ...	26.85	28.10	24.05	24.85	21.55	19.00	17.15	17.40	12.90	16.30

Very little hydrogen is present in any of the fractions; none at all could be detected in the tenth. The gases consist almost entirely of the paraffin hydrocarbons, the methane increasing at the expense of the higher members of the series as distillation proceeds.

Distillation at 950°:

TABLE II.

Rate of Evolution of Gas on Distillation at 950°.

Period No. 1.	During 1st 5 seconds.		16.05 c.c. measured at 0° and 760 mm.	
" 2	"	next 5	"	21.70
" 3	"	" 5	"	25.50
" 4	"	" 5	"	30.20
" 5	"	" 5	"	34.90
" 6	"	" 5	"	32.10
" 7	"	" 5	"	32.10
" 8	"	" 10	60.40 (about 30 c.c. per 5 sec.)	
" 9	"	" 15	"	70.70 " 23 "
" 10	"	" 30	"	56.60 " 9 "

TABLE III.

Percentage Composition of Gas Evolved during Different Time-intervals at 950°.

Calculated as "nitrogen-free" gas.

Period No. (1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).
Duration of heating, seconds.	5	5	5	5	5	5	10	15	30
C ₆ H ₆	9.45	7.45	6.85	6.60	4.80	4.10	2.45	1.60	0.20
CO ₂	2.35	2.65	2.80	2.45	1.25	1.80	1.60	1.60	0.30
C ₂ H ₂	1.45	1.15	1.20	0.85	1.05	1.00	0.55	nil.	0.30
C ₂ H ₄	6.85	4.35	5.50	4.65	4.05	2.80	1.35	0.75	0.20
CO.....	12.60	12.10	12.50	12.40	11.75	11.95	11.75	11.25	10.00
H ₂	11.35	23.85	30.75	33.50	33.95	39.00	48.95	62.30	77.75
CH ₄	44.55	37.65	32.90	31.05	34.75	32.75	28.50	20.55	10.10
C ₂ H ₆	11.40	10.85	7.55	8.45	8.40	6.35	5.05	2.00	0.80

TABLE IV.

*Volumes of Principal Constituents Evolved during Each Period.**

C.c. per 2 grams of dry coal.

Period No. (1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).
Duration of heating, seconds.	5	5	5	5	5	5	10	15	30
CO.....	2.08	2.63	3.19	3.74	4.10	3.84	3.75	8.55	7.07
H ₂	1.82	5.18	7.84	10.12	11.85	12.52	15.70	37.62	54.96
CH ₄	7.15	8.15	8.39	9.38	12.13	10.52	9.15	12.42	7.14
C ₂ H ₆	1.83	2.35	1.90	2.55	2.95	2.10	1.62	1.21	0.56

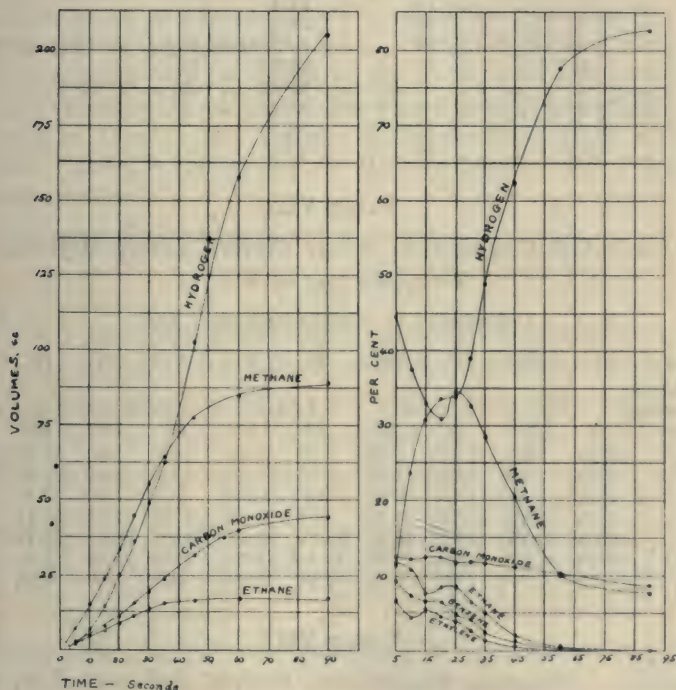
The numbers in these two tables are shown graphically in Fig. 3. It will be seen that the percentage of methane decreases as that of hydrogen increases, progressively from the beginning, until at

* These numbers, and those in similar tables, are calculated from the volumes of mixed gases evolved during each period and their percentage composition as analysed, not from the figures for the "nitrogen-free" gases given in the preceding table. The gases contained from 3 to 4 per cent. of nitrogen.

the end of 90 seconds the gases contain more than 80 per cent. of hydrogen, very little methane, and only traces of benzene, ethylene, and ethane. The rapidity with which the last three gases disappear is especially interesting in connexion with the question of the "illuminating power" of coal gas; for it is usually considered that the luminosity of coal gas is chiefly determined by their presence.

The curves showing the rate of evolution of the constituent gases indicate very clearly that the paraffin hydrocarbons are the primary

FIG. 3.

*Coal A. Distillation at 950°.*

(gaseous) decomposition products of the coal, whereas the main bulk of the hydrogen is a secondary product; for the evolution of ethane ceases entirely after the first 60 seconds, whilst the rate of evolution of methane has greatly diminished. The hydrogen, on the other hand, continues to be evolved fairly rapidly, and soon overtakes the methane.

Attention must also be directed towards the rate of evolution of carbon monoxide in this experiment. It will be observed that there

is very little fluctuation in the quantities evolved over periods of time of equal length.

Distillation at 900°:

The fractions were collected over longer intervals of time than in the preceding experiment.

TABLE V.

Rate of Evolution of Gas on Distillation at 900°.

Period No. 1.	During 1st 15 seconds.				55.0 c.c. at 0° and 760 mm.
" 2.	"	next 15	"	"	68.6
" 3.	"	" 15	"	"	72.4
" 4.	"	" 15	"	"	54.1
" 5.	"	" 30	"	"	70.5 (about 35 c.c. per 15 seconds).
" 6.	"	" 30	"	"	33.8 (" 16 ")
" 7.	"	" 1 minute.	"	"	22.0 (" 5 ")
" 8.	"	" 5 minutes.	"	"	32.8
" 9.	"	" 15	"	"	50.2
" 10.	"	" 30	"	"	13.5

TABLE VI.

Percentage Composition of Gas Evolved during Different Time-intervals at 900°.

Calculated as "nitrogen-free" gas.

Period No. (1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10)	
Duration of heating, seconds.	15	15	15	15	30	30	60	300	900	1800
C ₆ H ₆	13.10	7.60	4.25	1.10	0.85	0.40	0.35	nil	0.20	1.30
CO ₂	3.90	3.35	2.20	1.20	0.55	0.40	0.50	0.60	1.85	2.7
C ₂ H ₄	4.70	3.30	1.45	0.60	nil	nil	nil	0.20	0.40	0.2
CO	9.50	10.30	11.15	10.05	9.70	8.50	7.40	11.35	21.75	32.1
H ₂	10.35	32.15	45.15	66.00	74.55	83.45	84.85	82.35	70.45	50.4
CH ₄	46.00	41.60	28.20	19.10	18.45	6.75	6.90	5.50	5.05	13.2
C ₂ H ₆	12.45	1.70	7.20	1.95	0.90	0.50	nil	nil	0.30	ni

TABLE VII.

Volumes of Principal Constituents Evolved during Each Period.

C.c. per 2 grams of dry coal.

Period No. (1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10)	
Duration of heating, seconds.	15	15	15	15	30	30	60	300	900	1800
CO	5.23	7.06	8.07	5.42	6.84	2.88	1.54	3.72	10.92	4.0
H ₂	5.70	22.04	33.00	35.60	52.55	28.20	18.84	27.04	35.37	6.0
CH ₄	25.32	28.50	20.42	10.30	9.48	2.28	1.53	1.81	2.54	1.0
C ₂ H ₆	6.85	1.16	5.21	1.05	0.63	0.17	nil	nil	0.15	n

An increase in the percentage of carbon monoxide present successive distillations is very marked after the first eight minutes

corresponding increase in the percentage of carbon dioxide being also noticeable. The actual quantity evolved during equal intervals of time does not, however, increase in the same manner. Thus, taking one minute as the unit of time, the quantities evolved throughout the distillation were as follow:

Time from beginning of heating.	CO evolved during one minute.
1 minute.	25.78 c.c.
2 minutes.	9.72 "
3 "	1.64 "
8 "	0.75 "
23 "	0.73 "
53 "	0.14 "

Evolution of gas from the coal has, in fact, practically ceased at the end of twenty-three minutes; interaction between any steam formed and the coke remaining would continue, however, a mixture of carbon monoxide and hydrogen, with some carbon dioxide, being produced. It is to this reaction that we attribute the excess of carbon monoxide noticeable in the distillation during the last thirty minutes.

Fractional Distillation in a Vacuum:

TABLE VIII.

Total Volume and Percentage Composition of Gas obtained by Fractional Distillation in a Vacuum.

Volumes measured at 0° and 760 mm. Percentage composition as analysed.

Tempera- ture.	Vol- ume.	NH ₃ .	C ₆ H ₆ .	H ₂ S.	CO ₂ .	O ₂ .	C ₂ H ₂ .	C ₂ H ₄ .	CO.	H ₂ .	CH ₄ .	C ₂ H ₆ .	N ₂ .
15—35°	3.5	5.60	9.75	4.55	15.20	0.90	0.90	1.60	12.25	5.00	38.35		5.90
400°	18.0	2.25	14.10	1.50	3.15	0.10	0.55	3.50	4.95	13.40	27.75	26.90	1.85
450°	47.0	1.20	4.20	0.15	1.50	0.35	0.10	3.05	5.55	26.95	45.05	11.25	0.65
500°	59.5	1.10	2.85	0.80	1.45	0.20	0.20	1.10	7.65	40.50	41.20	1.00	1.95
550°	81.0	1.45	2.00	0.50	1.55	nil	nil	0.75	9.10	58.05	19.00	4.50	3.10
600°	98.0	0.50	0.75	0.30	1.20	0.35	0.20	0.10	8.75	70.05	12.45	2.35	3.00
650°	106.0	nil	0.25	0.15	1.30	0.05	0.05	0.15	7.40	76.05	6.98	0.95	7.20

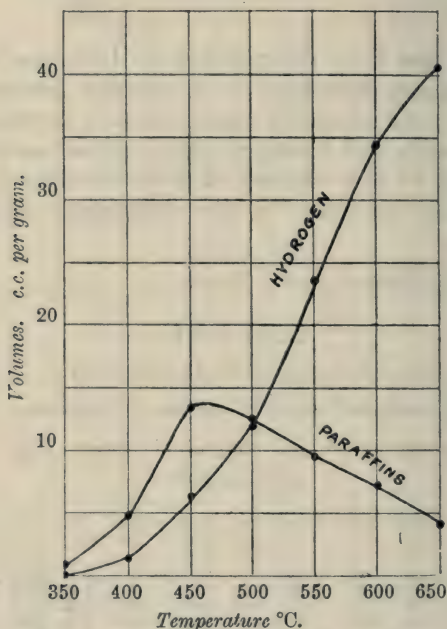
During the course of distillations in this manner there is a deposition of water along the cool neck of the glass retort. Since the coal used is dried at 107° during twenty-four hours when in the form of fine dust, it can safely be assumed that it is free from "pit-water," and that any that appears on distillation must be water of constitution, most probably arising from the elimination of hydroxyl groups.*

* In the course of further experiments on the behaviour of coal on distillation in a vacuum with the view of examining the liquid products, we have employed from 200—300 grams of finely pulverised coal dried during several days at 107°. A copious evolution of water occurs at about 200°, and can be condensed in a receiver cooled by solid carbon dioxide dissolved in ether.

The first fraction contains the occluded gases, decomposition of the coal only beginning to take place at about 350° , a fact which accounts for the high percentages of carbon monoxide and dioxide; for although the retort containing the coal is thoroughly evacuated at room temperature before beginning an experiment, occluded gases are sometimes retained, even at 150° .

The saturated hydrocarbons present in the first fraction obviously contained higher homologues than ethane, the ratio C/A on expo-

FIG. 4.



Coal A. Fractional Distillation in a Vacuum.

sion approximating closely to that required by propane ($C/A = 1.00$).

Continued evacuation during twenty-four hours suffices to extract completely all the gases that can be evolved at each temperature. The fact, therefore, that at 650° , after all the gases that can be evolved below that temperature have been removed, 76.05 per cent. of hydrogen and only 7.93 per cent. of saturated hydrocarbons are present, is strong confirmatory evidence of the existence of the two types of compounds indicated by the "period" distillations. This becomes more apparent on referring to the numbers in table IX, which gives the volumes of the constituent gases obtained at each

temperature, and on studying the curves obtained from these numbers in Fig. 4.

TABLE IX.

Volumes of Hydrogen and Saturated Hydrocarbons Evolved on Fractional Distillation in a Vacuum.

C.c. per 2 grams of dry coal.

Temperature.	15—350°	400°	450°	500°	550°	600°	650°
Hydrogen	0·15	2·40	12·65	24·10	47·00	68·65	80·60
Saturated hydrocarbons ...	1·35	9·85	26·95	25·10	19·05	14·50	8·40

Coal D (Semi-bituminous).

Distillation at 950°:

TABLE I.

Rate of Evolution of Gas on Distillation at 950°.

Period No. 1.	During 1st 15 seconds.	76·00 c.c. at 0° and 760 mm.
" 2.	" next 15 "	90·25
" 3.	" " 15 "	78·85
" 4.	" " 15 "	77·90
" 5.	" " 30 "	81·70 (about 40 c.c. per 15 seconds).
" 6.	" " 30 "	33·25 (" 16 " ").
" 7.	" " minute.	23·75 (" 11 " ").

TABLE II.

Percentage Composition of Gas Evolved during Different Time-intervals at 950°.

Calculated as "nitrogen-free" gas.

Period No. Duration of heating, seconds.	(1).	(2).	(3).	(4).	(5).	(6).	(7).
	15	15	15	15	30	30	60
NH ₃	1·50	0·35	0·20	0·10	0·10	0·10	nil
C ₆ H ₆	2·40	0·80	0·05	1·00	nil	nil	0·10
H ₂ S	0·95	0·10	nil	0·20	nil	nil	nil
CO ₂	3·45	0·90	0·35	0·20	0·20	0·10	0·10
C ₂ H ₄	nil	0·15	nil	nil	nil	nil	nil
CO	4·80	3·95	5·30	5·50	4·10	3·60	5·15
H ₂	35·45	56·40	76·80	84·40	90·30	91·40	89·80
CH ₄	42·85	34·60	15·00	8·20	4·10	3·55	4·25
C ₂ H ₆	6·00	1·75	2·15	0·35	1·20	1·20	0·60

TABLE III.

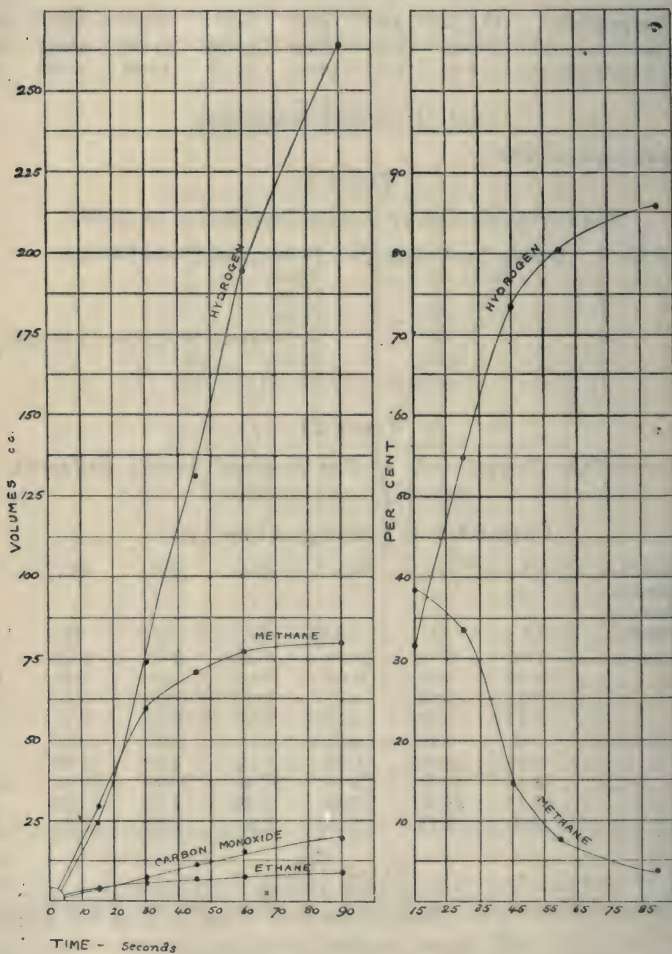
Volumes of Principal Constituents Evolved during Each Period.

C.c. per 2 grams of dry coal.

Period No. Duration of heating, seconds.	(1).	(2).	(3)	(4).	(5).	(6).	(7).
	15	15	15	15	30	30	60
H ₂	24·15	49·50	57·90	62·60	70·03	29·0	20·40
CH ₄	29·15	30·35	11·35	6·05	3·20	1·10	1·00
C ₂ H ₆	4·10	1·55	1·65	0·25	0·95	0·40	0·15

The figures in tables II and III are shown graphically in Fig. 5. Comparison with Fig. 3 shows that this coal contains a larger proportion of the hydrogen-yielding constituents than does the bituminous coal A. Some idea of the relative amounts of the

FIG. 5.



Coal D. Distillation at 950°.

paraffin-yielding constituents in the two coals is given by the quantities of paraffins evolved on heating in a vacuum up to 650°. In the case of coal A, the quantity is 53.3 c.c. per gram of ash-free dry coal; for coal D it is 44.2 c.c.

Fractional Distillation in a Vacuum:

TABLE IV.

Total Volume and Percentage Composition of Gas obtained by Fractional Distillation in a Vacuum.

Volumes measured at 0° and 700 mm. Percentage composition as analysed.

Tempera- ture.	Vol- ume, c.c.	NH ₃ .	C ₆ H ₆ .	H ₂ S.	CO ₂ .	O ₂ .	C ₂ H ₂ .	C ₂ H ₄ .	CO.	H ₂ .	CH ₄ .	C ₂ H ₆ .	N ₂
15—350°	0.95	2.50	1.60	5.15	51.70	1.60	nil	nil	19.10	8.00	nil.	6.35	4.00
450°	38.05	2.35	3.45	0.90	5.90	0.30	nil	1.40	5.80	31.80	32.90	10.65	4.55
550°	186.20	0.60	0.30	0.25	0.40	0.30	nil	0.55	2.80	69.40	19.55	3.00	2.85
600°	111.50	0.15	0.10	nil	0.25	0.25	nil	nil	5.90	80.00	8.65	1.80	2.90
650°	179.10	nil	nil	nil	0.15	nil	nil	nil	4.85	90.55	2.80	nil.	1.65

TABLE V.

Volumes of Hydrogen and Saturated Hydrocarbons Evolved on Fractional Distillation in a Vacuum.

C.c. per 2 grams of dry coal.

Temperature.	450°	550°	600°	650°
Hydrogen	12.1	129.2	89.2	162.2
Hydrocarbons.....	16.6	42.0	9.95	5.0

*Coal B (Anthracite).**Distillation at 900°:*

TABLE I.

Rate of Evolution of Gas on Distillation at 900°.

Period No. 1.	During 1st 5 seconds. 6.65 c.c. measured at 0° at 760 mm.			
„ 2	„ next 5	„	6.65	
„ 3	„ „ 5	„	9.50	
„ 4	„ „ 5	„	11.45	
„ 5	„ „ 5	„	15.24	
„ 6	„ „ 5	„	17.15	
„ 7	„ „ 5	„	17.15	
„ 8	„ „ 5	„	18.10	
„ 9	„ „ 5	„	17.15	
„ 10	„ „ 5	„	20.95	

TABLE II.

Percentage Composition of Gas Evolved during Different Time-intervals at 900°.

Calculated as "nitrogen-free" gas.

Period No.	(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).
NH ₃ ...	6.10	4.80	1.55	2.15	1.45	1.85	0.80	0.45	0.15	0.20
C ₆ H ₆ ...	3.80	2.10	2.30	0.15	0.90	0.20	0.25	0.10	0.15	0.35
H ₂ S	2.75	3.25	1.55	0.35	0.35	0.20	0.10	0.20	0.15	0.35
CO ₂	9.85	6.10	6.15	4.65	3.10	2.55	2.05	2.00	1.00	1.40
C ₂ H ₂ ...	0.30	0.40	0.15	nil	nil	0.20	0.15	nil	nil	nil
C ₂ H ₄ ...	2.35	0.75	nil	nil	nil	nil	nil	0.15	nil	nil
CO	16.65	11.90	9.75	7.30	8.85	7.85	5.55	3.70	6.25	5.60
H ₂	31.20	41.25	52.40	57.10	59.15	62.80	70.95	74.95	80.65	82.30
CH ₄	25.95	28.15	24.70	26.60	23.90	23.10	20.10	17.60	10.45	8.40
C ₂ H ₆ ...	1.10	1.30	1.45	1.65	2.10	1.25	nil	0.80	1.25	1.35

TABLE III.

Period No.	(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10)
Duration of heating, seconds.	5	5	5	5	5	5	5	5	5	5
CO	1.10	0.79	0.75	0.85	1.35	1.35	0.95	0.67	1.07	1.17
H ₂	2.07	2.74	4.97	6.55	9.01	10.75	12.15	13.56	13.82	17.24
CH ₄	1.72	1.87	2.35	3.83	3.65	3.95	3.45	3.19	1.80	1.76

TABLE IV.

Total Volumes and Percentage Composition of Gas obtained by Fractional Distillation in a Vacuum.

Volumes measured at 0° and 760 mm. Percentage composition as analysed.

Temperature.	Vol- ume, c.c.	NH ₃ .	C ₆ H ₆ .	H ₂ S.	CO ₂ .	O ₂ .	C ₂ H ₂ .	C ₂ H ₄ .	CO.	H ₂ .	CH ₄ .	C ₂ H ₆ .	N ₂ .
15—400°	2.55	2.90	3.00	6.45	50.45	3.45	nil.	1.10	16.20	4.30	8.85	nil	3.30
500°	15.30	2.20	1.75	0.65	7.45	0.45	0.20	nil	7.35	37.10	37.05	1.65	4.15
600°	118.00	1.05	0.60	0.60	1.65	0.30	0.40	nil	4.85	70.00	16.25	0.45	3.85

On comparing the results obtained from these three typical samples of bituminous, semi-bituminous, and anthracite coals, it is evident that their difference in behaviour on heating is mainly due to the different proportions of paraffin- and hydrogen-yielding constituents present in them. The sample of anthracite differs, however, from the others in being much denser, and therefore parting with its gases less readily. This was very noticeable during fractional distillation in a vacuum, continuous exhaustion during several days failing to remove the last traces of gas at each temperature, whereas with the other samples twelve hours was quite sufficient.

It is in comparison of samples of coal of the same class, however,

that the more interesting variations in composition are observed. In the course of an investigation directed towards determining the relative degrees of inflammability of the dusts from different coals, we have examined a number of bituminous coals. We give below the figures showing the relative quantities of paraffin-yielding constituents present in four different samples, and also the percentages of total "volatile matter" contained in each. The relative quantities of paraffin-yielding constituents are given by the volumes of paraffins evolved per gram of ash-free dry coal on heating in a vacuum up to 650°, at which temperature their evolution practically ceases.

Coal No.	Total volatile matter, per cent. of ash-free dry coal.	Paraffins evolved in a vacuum up to 650°, c.c. per gram of ash-free dry coal.
1.	40·60	47·9
2.	35·50	53·3
3.	33·07	62·7
4. ..	30·10	47·2

One coal may, therefore, contain a larger percentage of total volatile constituents than another, and yet not yield so great a quantity of paraffins. That is to say, it may not contain so much of the readily decomposed constituents.

We do not propose to discuss here the question of the influence of the chemical composition of coal on the inflammability of the dust from it, but may incidentally remark that for dusts of the same degree of fineness the ease with which inflammation can be propagated appears to be dependent on the percentage of paraffin-yielding constituents present in the coal, and not, as is sometimes supposed, on the total quantity of volatile constituents. This seems to us to afford an explanation of some of the anomalous results that have been obtained by different investigators who have tried to establish a relationship between the explosive properties of a dust and its chemical composition. It is an explanation which was foreshadowed by the Prussian Firedamp Commission (*Anlagen zur Haupt-Berichte der Preussischen Schlagwetter-Commission, Band IV*), who, arguing upon Muck's work, in which he showed that it is not always the coals containing the highest percentage of volatile matter that evolve their gas most rapidly when heated, but very often those of mean percentage, advanced the suggestion that it was not the actual percentage of volatile matter present, but rather the rapidity with which it was disengaged by heat, that determined the inflammability of the dust.

LXXIV.—*A New Synthesis of 4(or 5)- β -Aminoethylglyoxaline, one of the Active Principles of Ergot.*

By FRANK LEE PYMAN.

BARGER and Dale (Trans., 1910, **97**, 2592) have recently shown that 4(or 5)- β -aminoethylglyoxaline (β -iminazolyethylamine) occurs in certain aqueous extracts of ergot, and Dale and Laidlaw (*J. Physiol.*, 1910, **41**, 318) have shown that its physiological activity is very great.

This base was first prepared by Windaus and Vogt (*Ber.*, 1907, **40**, 3691), who synthesised it from glyoxaline-4(or 5)-propionic acid through the hydrazide, azide, and urethane by Curtius's method. Glyoxaline-4(or 5)-propionic acid is obtained synthetically only in poor yield by the action of formaldehyde and ammonia on glyoxylpropionic acid (Knoop and Windaus, *Beitr. chem. Physiol. Path.*, 1905, **7**, 144), but may more readily be prepared from the naturally-occurring amino-acid histidine (*l*- α -amino- β -glyoxaline-4(or 5)-propionic acid); the latter is, however, a somewhat expensive compound, and 4(or 5)- β -aminoethylglyoxaline is, therefore, not readily accessible by this method.

Recently, this base has been prepared directly from histidine by the elimination of carbon dioxide, both by bacterial action (Ackermann, *Zeitsch. physiol. Chem.*, 1910, **65**, 504), and by chemical methods (Ewins and Pyman, this vol., p. 339).

No other method for the preparation of the base has hitherto been described, and its production has, therefore, practically depended on a supply of the naturally occurring amino-acid histidine.

In view of the possible therapeutic importance of this base, it seemed, therefore, important to devise some method by which it could conveniently be synthesised from readily available material, and the following method was found to be suitable. The method is based on Gabriel's discovery (*Ber.*, 1893, **26**, 2204; 1894, **27**, 1037) that amino-ketones of the general formula $R \cdot CO \cdot CH_2 \cdot NH_2$ yield, on condensation with potassium thiocyanate, thioglyoxalines of the general formula

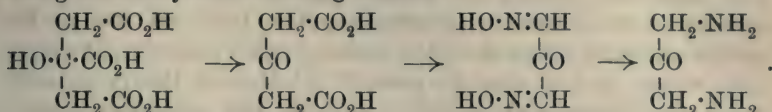
$$R \cdot \overset{\overset{CH \cdot NH}{\parallel}}{\underset{\underset{N}{\parallel}}{C}} \triangleright C \cdot SH,$$

which may be oxidised by nitric acid to glyoxalines of the type

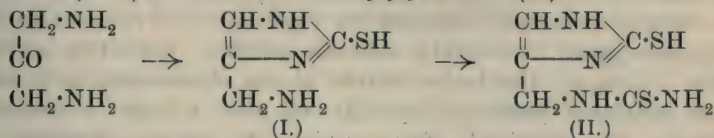
$$R \cdot \overset{\overset{CH \cdot NH}{\parallel}}{\underset{\underset{N}{\parallel}}{C}} \triangleright CH.$$

Diaminoacetone dihydrochloride formed the starting material for this synthesis, and this compound is readily prepared from citric acid, through acetonedicarboxylic acid and diisonitrosoacetone by

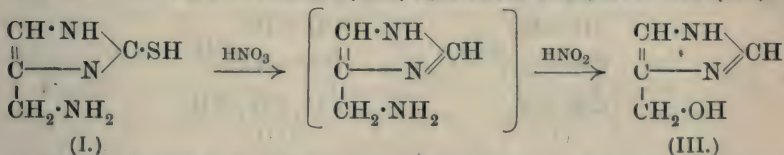
Kalischer's method (*Ber.*, 1895, **28**, 1519), the course of the reaction being shown by the following scheme:



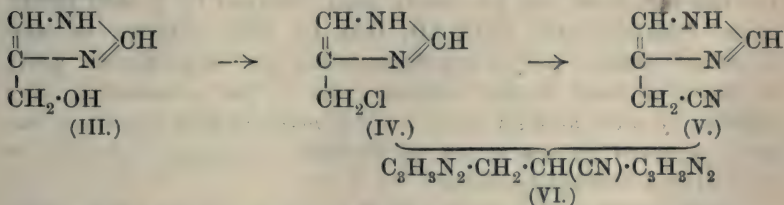
Diaminoacetone dihydrochloride, when heated with one molecular proportion of potassium thiocyanate, readily yields 2-thiol-4(or 5)-aminomethylglyoxaline (I), together with small quantities of 2-thiol-4(or 5)-thiocarbamidomethylglyoxaline (II):



On oxidising the former compound with nitric acid, the thiol sulphur is removed as sulphuric acid, and a glyoxaline results, as in Gabriel's experiments, but the free nitrous acid formed in the reaction attacks the amino-group, replacing it by a hydroxyl group, and the resulting product is 4(or 5)-hydroxymethylglyoxaline (III):



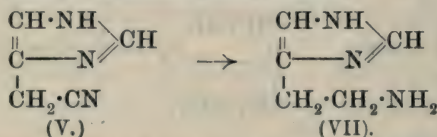
The hydrochloride of this base gives with phosphorus pentachloride an excellent yield of the hydrochloride of 4(or 5)-chloromethylglyoxaline (IV), and this salt, when dissolved in alcohol and dropped into an ice-cold, saturated aqueous solution of potassium cyanide, gives a 50 per cent. yield of 4(or 5)-cyanomethylglyoxaline (V). The latter base, however, is accompanied by a quantity of $\alpha\beta$ -bis[4(or 5)-glyoxaline]-propionitrile (VI), besides a considerable quantity of oily by-products, which have not yet been further examined:



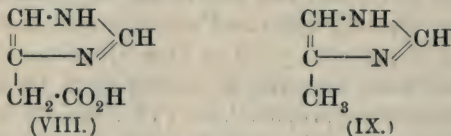
The formation of the last-named compound is, no doubt, due to the condensation of a molecule of the cyano-compound with a molecule of the chloro-compound; it is analogous to the formation

of $\alpha\beta$ -bis(*o*-nitrophenyl)propionitrile when *o*-nitrobenzyl chloride and potassium cyanide are boiled together for several hours in aqueous alcoholic solution (Bamberger, *Ber.*, 1886, **19**, 2635). The conditions under which the latter reaction takes place are, of course, more severe, and it may be pointed out that in the preparation of phenylacetone nitrile from benzyl chloride and potassium cyanide prolonged boiling in aqueous alcoholic solution is also necessary. The extraordinary reactivity of 4(or 5)-chloromethylglyoxaline, indicated by the ease with which the halogen is replaced, emphasises the marked influence of the glyoxaline complex on the side-chain. An attempt was made to effect the replacement of the chloro- by the cyano-group in absolute alcoholic solution, but after several hours' boiling of the hydrochloride of the chloro-compound with finely powdered potassium cyanide in this solvent, a complex mixture was obtained, from which a certain amount of 4(or 5)-ethoxymethylglyoxaline, $C_3H_3N_2 \cdot CH_2 \cdot OEt$, but none of the cyano-compound, could be isolated.

The last stage of the synthesis of 4(or 5)- β -aminoethylglyoxaline (VII) was accomplished by the reduction of 4(or 5)-cyanomethylglyoxaline by means of sodium and alcohol:



when there were also obtained as by-products a large amount of glyoxaline-4(or 5)-acetic acid (VIII) and a small quantity of 4(or 5)-methylglyoxaline (IX):



Glyoxaline-4(or 5)-acetic acid, which is thus prepared synthetically for the first time, has previously been obtained by Knoop (*Beitr. chem. Physiol. Path.*, 1907, **10**, 119) by the oxidation of oxydeaminohistidine (α -hydroxy- β -glyoxaline-4(or 5)-propionic acid). It has now been further characterised by the preparation of a number of salts, and its ester, *ethyl glyoxaline-4(or 5)-acetate*, has been prepared by the action of alcoholic hydrogen chloride on 4(or 5)-cyanomethylglyoxaline.

The occurrence of 4(or 5)-methylglyoxaline amongst the reduction products of 4(or 5)-cyanomethylglyoxaline is probably due to the loss of carbon dioxide on the part of glyoxaline-4(or 5)-acetic acid.

It was thought possible that the yield of 4(or 5)- β -aminoethylglyoxaline might be increased by converting the cyano-compound into the corresponding thioamide, and reducing this with zinc and dilute hydrochloric acid, a method advantageously employed by Hofmann (*Ber.*, 1868, **1**, 102), and subsequently by Bamberger and Lodter (*Ber.*, 1888, **21**, 51) in the formation of bases of the type $R \cdot CH_2 \cdot NH_2$ from cyanides $R \cdot CN$, where R is an aryl radicle; in the present case, however, whilst *glyoxaline*-4(or 5)-*acet-thioamide*, $C_3H_3N_2 \cdot CH_2 \cdot CS \cdot NH_2$, was formed almost quantitatively from 4(or 5)-cyanomethylglyoxaline and alcoholic ammonium sulphide, its reduction led to mere traces of the required product.

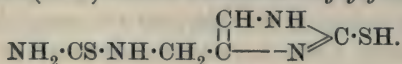
In conclusion, it may be mentioned that several of the new glyoxaline derivatives described in this communication form suitable starting points for the synthesis of more complicated substances containing the glyoxaline ring, and it is proposed to attempt the synthesis of such compounds, in particular of those which occur in nature, namely, histidine and pilocarpine.

EXPERIMENTAL.

The Action of Potassium Thiocyanate on Diaminoacetone.

Fifty grams of diaminoacetone dihydrochloride were added to a hot solution of 30 grams of potassium thiocyanate in 50 c.c. of water, and the mixture was heated in the steam-bath. At first, a clear solution was obtained, but after about ten minutes crystals began to separate. After heating for about one hour, no further quantity of crystals appeared to be formed, and after heating for another half-hour, the liquor was cooled and the crystals collected (mother liquor *M*). On boiling the crystals with 75 c.c. of water, the bulk passed into solution, but 1.2 grams of 2-thiol-4(or 5)-thiocarbamidomethylglyoxaline, melting at 233° (uncorr.), remained undissolved, and were collected.

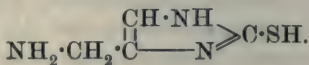
The filtrate was then mixed with a solution of 21 grams of anhydrous potassium carbonate in 75 c.c. of water, somewhat evaporated, and set aside, when 8.2 grams of 2-thiol-4(or 5)-aminomethylglyoxaline, melting at 188°, separated. To the mother liquor from this crop of crystals the mother liquor *M* was added, and the mixture evaporated to dryness under diminished pressure and extracted with alcohol. After removing the solvent from the alcoholic extract and diluting the resulting dark brown oil with a little water, further crops of nearly pure 2-thiol-4(or 5)-aminomethylglyoxaline, amounting to 17.9 grams, were obtained. The total yield of this base—26.1 grams—represents 64 per cent. of the theoretical.

2-Thiol-4(or 5)-thiocarbamidomethylglyoxaline,

This compound crystallises from boiling water in small, transparent, isolated prisms, which melt and decompose at 237—238° (corr.). It is anhydrous, and is very sparingly soluble in boiling water or alcohol. It is insoluble in dilute hydrochloric acid, but soluble in aqueous sodium hydroxide:

0.1533 gave 0.1807 CO₂ and 0.0607 H₂O. C=32.1; H=4.4.

C₅H₈N₄S₂ requires C=31.9; H=4.3 per cent.

2-Thiol-4(or 5)-aminomethylglyoxaline,

This base crystallises from water or alcohol in large, clear, colourless, quadrilateral plates, which melt and decompose at 188° (corr.). It is anhydrous, and is moderately easily soluble in cold water, sparingly so in cold absolute alcohol, but very easily so in hot water. It is sparingly or very sparingly soluble in the other usual organic solvents, even when hot. Aqueous solutions of the base yield with silver nitrate solution a precipitate in the form of a fine, yellow powder, which is not affected by ammonia, but becomes white on the addition of dilute nitric acid; such solutions give a white, amorphous precipitate with aqueous mercuric chloride or a solution of zinc hydroxide in ammonia, and an intense red coloration on the addition of sodium diazobenzene-*p*-sulphonate:

0.1538 gave 0.2079 CO₂ and 0.0783 H₂O. C=36.9; H=5.7.

0.0744 „ 20.6 c.c. N₂ at 21° and 764 mm. N=32.3.

C₄H₇N₃S requires C=37.2; H=5.5; N=32.5 per cent.

The *hydrochloride* crystallises from water in crusts formed by rosettes of needles. This salt darkens at 265°, and is quite charred at 270° (corr.), when it shrinks somewhat, but does not melt. It is anhydrous, and easily soluble in cold water, giving a solution neutral to litmus:

0.1531 gave 0.1647 CO₂ and 0.0685 H₂O. C=29.3; H=5.0.

0.1615 „ 0.1737 CO₂ „ 0.0735 H₂O. C=29.3; H=5.1.

C₄H₇N₃S.HCl requires C=29.0; H=4.9 per cent.

The *picrate* crystallises from water in large, stout, serrated needles of an intense orange colour, which decompose at 237° (corr.). This salt is anhydrous, and is fairly easily soluble in hot water, but very sparingly so in cold:

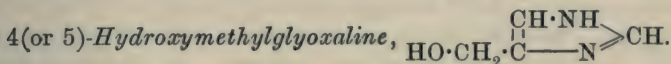
0.1541 gave 0.1898 CO₂ and 0.0438 H₂O. C=33.6; H=3.2.

0.1526 „ 0.1873 CO₂ „ 0.0445 H₂O. C=33.5; H=3.2.

C₄H₇N₃S, C₆H₃O₇N₃ requires C=33.5; H=2.8 per cent.

The Action of Nitric Acid on 2-Thiol-4(or 5)-aminomethylglyoxaline.

Fifteen grams of 2-thiol-4(or 5)-aminomethylglyoxaline were added gradually during twenty minutes to 300 c.c. of 10 per cent. aqueous nitric acid, which was kept gently boiling over a small flame. The clear, pale yellow liquor was then boiled for ten minutes, neutralised with aqueous sodium hydroxide, and mixed with a solution of 26.6 grams of picric acid in 600 c.c. of boiling water. On cooling, a large quantity of 4(or 5)-hydroxymethylglyoxaline picrate separated, and further crops were obtained on concentration. The salt was purified by crystallisation from water, and 27.9 grams of the pure picrate were obtained; the yield thus amounted to 74 per cent. of the theoretical.



This base may be obtained from its picrate by shaking the latter with dilute hydrochloric acid and ether until the picric acid is removed, adding to the resulting solution of the hydrochloride an excess of sodium carbonate, evaporating to dryness under diminished pressure, and extracting with absolute alcohol. It crystallises from absolute alcohol in large, clear, colourless hexahedra, which melt at 93—94° (corr.). It is very easily soluble in water, easily so in absolute alcohol, but sparingly so in the other usual organic solvents. It cannot be distilled under 20 mm. pressure, but suffers decomposition:

0.1519 gave 0.2717 CO₂ and 0.0844 H₂O. C=48.8; H=6.2.

0.1010 „ 24.6 c.c. N₂ at 22° and 767 mm. N=28.4.

C₄H₆ON₂ requires C=49.0; H=6.2; N=28.6 per cent.

Aqueous solutions of this base give with mercuric chloride, ammoniacal silver nitrate, and ammoniacal solution of zinc hydroxide, white, amorphous precipitates; with sodium diazobenzene-*p*-sulphonate, an intense red coloration.

The *hydrochloride* crystallises from absolute alcohol in long, flat, prismatic needles, which melt at 107—109° (corr.), after sintering from 105°. It is very deliquescent, and very easily soluble in water or alcohol:

0.1542* gave 0.2019 CO₂ and 0.0778 H₂O. C=35.7; H=5.7.

0.1383* „ 0.1820 CO₂ „ 0.0702 H₂O. C=35.9; H=5.7.

* Dried at 100°.

0.0855* gave 15.3 c.c. N_2 at 18° and 751 mm. $N = 20.7$.

0.1587* „ 0.1700 AgCl. $Cl = 26.5$.

$C_4H_6ON_2 \cdot HCl$ requires $C = 35.7$; $H = 5.3$; $N = 20.9$;
 $Cl = 26.3$ per cent.

The *nitrate* crystallises from absolute alcohol in wedge-shaped, transparent plates, which melt at $84-86^\circ$ (corr.), after sintering a few degrees earlier. It is deliquescent, very easily soluble in water or hot absolute alcohol, and easily so in cold absolute alcohol:

0.1399* gave 0.1526 CO_2 and 0.0580 H_2O . $C = 29.7$; $H = 4.6$.

$C_4H_6ON_2 \cdot HNO_3$ requires $C = 29.8$; $H = 4.3$ per cent.

The *picrate* crystallises from water in glistening scales, which melt and decompose at 207° (corr.). It is anhydrous, and is fairly easily soluble in hot water, but very sparingly so in cold:

0.1388 gave 0.1862 CO_2 and 0.0401 H_2O . $C = 36.6$; $H = 3.2$.

$C_4H_6ON_2 \cdot C_6H_3O_7N_3$ requires $C = 36.7$; $H = 2.8$ per cent.

The *hydrogen oxalate* crystallises from water in large, clear, colourless prisms, which contain one molecule of water of crystallisation, and have no sharp melting point, commencing to sinter at 80° , and gradually liquefying between this temperature and 100° . After drying, first at about 50° , then at 100° , this salt melts at $134-136^\circ$ (corr.). It is soluble in about four parts of cold water, and very easily soluble in hot water:

0.1500† gave 0.1906 CO_2 and 0.0662 H_2O . $C = 34.7$; $H = 4.9$.

0.2118† lost 0.0182 at 100° . $H_2O = 8.6$.

$C_4H_6ON_2 \cdot C_2H_2O_4 \cdot H_2O$ requires $C = 34.9$; $H = 4.9$; $H_2O = 8.7$

0.1488* gave 0.2072 CO_2 and 0.0545 H_2O . $C = 38.0$; $H = 4.1$.

$C_4H_6ON_2 \cdot C_2H_2O_4$ requires $C = 38.3$; $H = 4.3$ per cent.

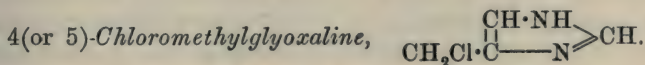
The Action of Phosphorus Pentachloride on 4(or 5)-Hydroxymethylglyoxaline.

To 57 grams of phosphorus pentachloride contained in a round-bottomed flask, 36.5 grams of 4(or 5)-hydroxymethylglyoxaline hydrochloride were added in small portions, with thorough shaking, in the course of a few minutes. Copious fumes of hydrogen chloride were evolved, and the reaction mass quickly became a viscous liquid, and then solidified. Fifty c.c. of chloroform were then added, to wash any unchanged pentachloride into contact with unchanged hydroxy-compound, and the mixture was then heated on the water-bath, first under ordinary, and then under diminished, pressure to remove chloroform, hydrogen chloride, and phosphoryl chloride. The residue was then dissolved in about

* Dried at 100° .

† Air dried salt.

50 c.c. of hot absolute alcohol, and set aside, when 33.0 grams of 4(or 5)-chloromethylglyoxaline hydrochloride, melting at 140—142°, separated; on allowing the mother liquor to evaporate spontaneously in a desiccator, a further 2.8 grams of the same salt, in a fairly pure condition, were obtained. The total yield—35.8 grams—amounts to 86 per cent. of the theoretical, and further quantities were obtained by again treating the residual oil with phosphorus pentachloride.



The *hydrochloride* crystallises from absolute alcohol in prismatic needles or stout prisms, which melt at 144—145° (corr.). This salt is deliquescent, very easily soluble in water or hot absolute alcohol, and fairly easily so in cold absolute alcohol:

0.1531* gave 0.1750 CO_2 and 0.0558 H_2O . C=31.2; H=4.1.

0.1539* „ 0.2866 AgCl. Cl=46.1.

$\text{C}_4\text{H}_5\text{N}_2\text{Cl}\cdot\text{HCl}$ requires C=31.4; H=4.0; Cl=46.3 per cent.

Aqueous solutions of this salt remain clear on the addition of aqueous sodium carbonate, but become turbid, depositing a yellow oil soluble in excess, on the addition of aqueous sodium hydroxide.

The *picrate* is obtained in long, glistening, silky yellow needles, when a cold solution of picric acid is added to a freshly prepared solution of 4(or 5)-chloromethylglyoxaline hydrochloride in cold water. It is anhydrous, and melts and decomposes at 181° (corr.):

0.1434 gave 0.1810 CO_2 and 0.0334 H_2O . C=34.4; H=2.6.

$\text{C}_4\text{H}_5\text{N}_2\text{Cl}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires C=34.7; H=2.3 per cent.

On dissolving this salt in a little boiling water, and immediately cooling the solution, pure 4(or 5)-hydroxymethylglyoxaline picrate, melting at 207° (corr.), either alone or when mixed with the pure salt, separates.

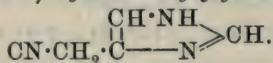
The Action of Aqueous Potassium Cyanide on 4(or 5)-Chloromethylglyoxaline.

A solution of 30 grams of 4(or 5)-chloromethylglyoxaline hydrochloride in 135 c.c. of absolute alcohol was added drop by drop to 90 grams of potassium cyanide in 100 c.c. of water, which was mechanically stirred and kept at about 0°, the addition occupying approximately thirty minutes. The mixture was then filtered, and the potassium salts washed with alcohol. The filtrate and washings were combined, mixed with 180 c.c. of 10 per cent. aqueous sodium

* Dried at 100°.

carbonate, and evaporated to dryness under diminished pressure. The residue was extracted with warm ethyl acetate, and the extract distilled, when 16.3 grams of a brown oil remained. This began to crystallise, and after dissolution in a little warm water, 7.5 grams of pure 4(or 5)-*cyanomethylglyoxaline* separated, and a second crop of 1.0 gram of the cyano-base was obtained on concentrating the mother liquor. The oily liquor remaining was then converted into the acid oxalate by the addition of 9 grams of oxalic acid, and the resulting crops of mixed oxalates fractionally crystallised from water, when small quantities of 4(or 5)-*cyanomethylglyoxaline* acid oxalate and $\alpha\beta$ -bis[4(or 5)-*glyoxaline*]-*propionitrile hydrogen oxalate* were obtained. These oxalates, however, readily crystallise out side by side, and their separation is tedious. The total yield of 4(or 5)-*cyanomethylglyoxaline* amounts to about 50 per cent. of the theoretical.

4(or 5)-*Cyanomethylglyoxaline*,



This base crystallises from water or ethyl acetate in stout, prismatic needles, which sinter at 136°, soften at 137°, and melt to a clear liquid at 138—140° (corr.). It is sparingly soluble in ether, chloroform, benzene, light petroleum, or cold water, but easily so in ethyl acetate, acetone, alcohol, or hot water:

0.1339 gave 0.2755 CO₂ and 0.0573 H₂O. C=56.1; H=4.8.

0.0673 „ 22.5 c.c. N₂ at 19° and 770 mm. N=39.6.

C₅H₅N₃ requires C=56.0; H=4.7; N=39.2 per cent.

Aqueous solutions of this base give with mercuric chloride, ammoniacal silver nitrate, and ammoniacal solution of zinc hydroxide, white, amorphous precipitates; with sodium diazo-benzene-*p*-sulphonate, a dirty brownish-red colour, very much more intense than the beautiful red colour given by other glyoxalines containing a free imino-hydrogen atom, is produced; the difference is probably due to the product containing two chromophoric groups, one of which is attached to the imino-group as in other glyoxalines, and the second to the methylene group which is situated between the glyoxaline complex and the cyano-group.

The *hydrochloride* crystallises from absolute alcohol in thin, glistening leaflets, which melt at 168—169° (corr.). It is very easily soluble in water, and fairly easily so in boiling absolute alcohol, but sparingly so in the latter when cold:

0.1514 gave 0.2315 CO₂ and 0.0585 H₂O. C=41.7; H=4.3.

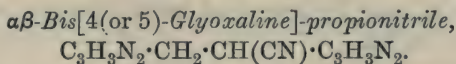
C₅H₅N₃.HCl requires C=41.8; H=4.2 per cent.

The *hydrogen oxalate* crystallises from water in crusts consisting of indefinite prisms. This salt decomposes at 194° (corr.), and is easily soluble in hot water, but sparingly so in cold:

0.1542 gave 0.2403 CO_2 and 0.0546 H_2O . $\text{C}=42.5$; $\text{H}=4.0$.

$\text{C}_5\text{H}_5\text{N}_3, \text{C}_2\text{H}_2\text{O}_4$ requires $\text{C}=42.6$; $\text{H}=3.6$ per cent.

The *picrate* crystallises from water in yellow leaflets, which begin to sinter at 155° , and melt at 165 — 166° (corr.). It is sparingly soluble in cold water or alcohol.



The *hydrogen oxalate* crystallises from water in stout, clear, prismatic needles, which melt and decompose at 181 — 182° (corr.). It is anhydrous and somewhat sparingly soluble in cold water, but easily so in hot water:

0.1528 gave 0.2288 CO_2 and 0.0477 H_2O . $\text{C}=40.8$; $\text{H}=3.5$.

0.1052 „ 15.2 c.c. N_2 at 18° and 769 mm. $\text{N}=17.2$.

$(\text{C}_9\text{H}_{10}\text{N}_5)_2, 5\text{C}_2\text{H}_2\text{O}_4$ requires $\text{C}=40.7$; $\text{H}=3.7$; $\text{N}=17.0$;

$\text{C}_2\text{H}_2\text{O}_4=54.5$ per cent.

On dissolving 2.05 grams of this salt in water, and adding an excess of barium hydroxide solution, 2.8 grams of barium oxalate, corresponding with 54.6 per cent. of oxalic acid were collected; the filtrate from this, after treatment with carbon dioxide and removal of barium carbonate, was evaporated to dryness, when a colourless varnish remained. This was readily soluble in water, giving an alkaline solution, and when acidified with hydriodic acid and evaporated to low bulk, gave a beautifully crystalline hydriodide.

The *hydriodide* crystallises from water in well-formed rhombic prisms, which melt at 200 — 201° (corr.). It is sparingly soluble in cold water or alcohol, and is anhydrous:

0.1539 gave 0.1932 CO_2 and 0.0467 H_2O . $\text{C}=34.2$; $\text{H}=3.4$.

0.1472 „ 27.4 c.c. N_2 at 14° and 768 mm. $\text{N}=22.4$.

0.2030 „ 0.1496 AgI . $\text{I}=39.8$.

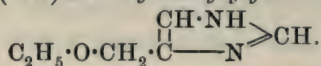
$\text{C}_9\text{H}_{10}\text{N}_5, \text{HI}$ requires $\text{C}=34.2$; $\text{H}=3.5$; $\text{N}=22.2$; $\text{I}=40.1$ per cent.

The Action of Alcoholic Potassium Cyanide on 4(or 5)-Chloromethylglyoxaline.

Ten grams of 4(or 5)-chloromethylglyoxaline hydrochloride, 12 grams of finely powdered potassium cyanide, and 40 c.c. of absolute alcohol were boiled together under a reflux condenser for five and a-half hours. The mixture was then filtered from the potassium salts, and these washed with alcohol; the filtrate was rendered

alkaline with 80 c.c. of 10 per cent. aqueous sodium carbonate, and evaporated to dryness under diminished pressure. The residue was thoroughly extracted with ether, and gave 5.6 grams of pale yellow oil; this was mixed with its own weight of oxalic acid, and the acid oxalates fractionally crystallised from water, when 3.4 grams of pure 4(or 5)-*ethoxymethylglyoxaline hydrogen oxalate* were obtained; besides this oxalate, which separates first in large crystals, other crystalline oxalates were present in the mother liquors. No 4(or 5)-cyanomethylglyoxaline hydrogen oxalate could be isolated from them by fractional crystallisation, and they were not further examined.

4(or 5)-*Ethoxymethylglyoxaline*,



This base is liberated from the oxalate by treating the latter with baryta, filtering from barium oxalate, and removing the excess of baryta as carbonate. It crystallises from anhydrous ether in prismatic needles, which sinter from 50°, and melt at 53–55° (corr.).

It is easily soluble in water, and the usual organic solvents, with the exception of light petroleum:

0.1530 gave 0.3219 CO₂ and 0.1097 H₂O. C=57.4; H=8.0.

0.1533 „ 0.3199 CO₂ „ 0.1094 H₂O. C=56.9; H=8.0.

C₆H₁₀ON₂ requires C=57.1; H=8.0 per cent.

The *hydrogen oxalate* crystallises from water in large prisms, which melt at 165–167° (corr.). It is anhydrous, and is soluble in about 4 parts of cold water, but readily so in hot water:

0.1563 gave 0.2668 CO₂ and 0.0839 H₂O. C=46.6; H=6.0.

0.1443 „ 0.2457 CO₂ „ 0.0794 H₂O. C=46.4; H=6.2.

0.1274 „ 16.0 c.c. N₂ at 21° and 754 mm. N=14.5.

(C₆H₁₀ON₂)₄.(C₂H₂O₄)₃ requires C=46.5; H=6.0; N=14.6 per cent.

The Reduction of 4(or 5)-Cyanomethylglyoxaline. Preparation of 4(or 5)- β -Aminoethylglyoxaline.

Ten grams of 4(or 5)-cyanomethylglyoxaline were dissolved in 50 c.c. of absolute alcohol, and 25 grams of sodium added piece by piece within a few minutes. Further quantities of hot absolute alcohol were added a few c.c. at a time, while the mixture was heated by a small flame, until after the addition of about 200 c.c. of absolute alcohol (making 250 c.c. in all) in the course of an hour and a-quarter, nearly all the sodium had dissolved. A little

water was then added to remove the last traces of sodium, and the liquor was acidified by the addition of 120 c.c. of concentrated hydrochloric acid. After removing the sodium chloride, and washing this with alcohol, the filtrate was evaporated to low bulk, mixed with 100 c.c. of cold saturated aqueous sodium carbonate, and evaporated to complete dryness under diminished pressure. The residue was then extracted with absolute alcohol, which removed all the organic matter, and the extract was concentrated to about 50 c.c., when, on cooling, 4.65 grams of crude *sodium glyoxaline-4(or 5)-acetate* were deposited as a crystalline powder, which was collected, washed with absolute alcohol, and reserved. The alcoholic mother liquor left on evaporation about 8 grams of a viscid brown oil. This was dissolved in a little water, and added to a boiling solution of 30 grams of picric acid in one litre of water. On cooling, a quantity of 4(or 5)- β -aminoethylglyoxaline dipicrate crystallised out, mixed with a little dark brown resinous matter; after recrystallisation from water, the latter was removed, and 14.6 grams of pure dipicrate were obtained.

4(or 5)- β -Aminoethylglyoxaline dipicrate, either alone or mixed with the salt prepared from histidine (Ewins and Pyman, *loc. cit.*), melted and decomposed at 238—242° (corr.), according to the rate of heating:

0.1487 gave 0.1946 CO₂ and 0.0375 H₂O. C=35.7; H=2.8.

C₅H₉N₃.(C₆H₃O₇N₃)₂ requires C=35.8; H=2.7 per cent.

It was further identified by converting it into the dihydrobromide which melted and decomposed at 284° (corr.):

0.1541 gave 0.1232 CO₂ and 0.0578 H₂O. C=21.8; H=4.2.

C₅H₉N₃.2HBr requires C=22.0; H=4.1 per cent.

Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, kindly tested a specimen of this synthetic 4(or 5)- β -aminoethylglyoxaline dipicrate, and found that it had the physiological activity of the pure salt prepared from histidine.

After the separation of the dipicrate, the mother liquors deposited first a crystalline picrate, melting at about 160—170°, and then a sticky oil; these fractions, on extraction with a little warm alcohol, gave 0.6 gram of 4(or 5)- β -aminoethylglyoxaline dipicrate as a sparingly soluble residue. This was collected, and all the picrate mother liquors—alcoholic and aqueous—were then combined and boiled to remove the alcohol. The clear hot solution was mixed with concentrated hydrochloric acid, cooled, filtered from picric acid, and extracted with ether to remove the remainder of the latter. The resulting solution of hydrochlorides was made alkaline with sodium carbonate, evaporated to complete dryness

under diminished pressure, and extracted first with ether, then with absolute alcohol.

From the ethereal extract, 1.0 gram of nearly colourless, viscid oil was obtained. This was converted into the picrate, and crystallised first from water, then from alcohol, when 1.35 grams of pure 4(or 5)-methylglyoxaline picrate were isolated. This salt melted at 160—162° (corr.), both alone and when mixed with the salt prepared from the pure base; the latter salt had the same melting point. Windaus and Knoop (*Ber.*, 1905, **38**, 1170) give 159—160°:

0.1471 gave 0.2074 CO₂ and 0.0397 H₂O. C=38.5; H=3.0.

0.1028 „ 19.4 c.c. N₂ at 13° and 775 mm. N=23.0.

C₄H₆N₂·C₆H₃O₇N₃ requires C=38.6; H=2.9; N=22.5 per cent.

The alcoholic extract left, on evaporation, 1.2 grams of crude crystalline sodium 4(or 5)-glyoxaline acetate; this was combined with the 4.65 grams which had separated earlier, neutralised with hydrochloric acid, and converted into the picrate, when 11.5 grams of pure glyoxaline-4(or 5)-acetic acid picrate, melting at 212—213° (corr.), were obtained. The yield of 4(or 5)- β -aminoethylglyoxaline—15.2 grams of the dipicrate—amounts to 29 per cent., and that of glyoxaline-4(or 5)-acetic acid to 35 per cent., of the theoretical.

Glyoxaline-4(or 5)-acetic Acid, C₃H₃N₂·CH₂·CO₂H.

This substance was obtained by treating its hydrochloride with silver carbonate, filtering from silver chloride, removing the excess of silver present as glyoxalineacetate by means of hydrogen sulphide, and concentrating the liquor to low bulk, when it separated in fan-shaped clusters of prismatic needles, which melt and decompose at 222° (corr.):

0.1613 lost 0.0201 at 100°. H₂O=12.5.

C₅H₆O₂N₂·H₂O requires H₂O=12.5 per cent.

0.1412 gave 0.2466 CO₂ and 0.0600 H₂O. C=47.6; H=4.8.

C₅H₆O₂N₂ requires C=47.6; H=4.8 per cent.

This acid has previously been prepared by Knoop (*Beitr. chem. Physiol. Path.*, 1907, **10**, 111) by the oxidation of oxydeamino-histidine, that is, α -hydroxy- β -glyoxaline-4(or 5)-propionic acid, C₃H₃N₂·CH₂·CH(OH)·CO₂H. He describes it as fan-shaped needles from aqueous acetone, which contain 1H₂O, and melt and decompose at 220°.

The *hydrochloride* crystallises from absolute alcohol in small needles, which melt and decompose at 225—226° (corr.), after sintering a few degrees earlier. It is anhydrous, and is very easily soluble in water, but sparingly so in alcohol:

0.1541 gave 0.2080 CO_2 and 0.0618 H_2O . $\text{C}=36.8$; $\text{H}=4.5$.

0.2002 „ 0.1767 AgCl . $\text{Cl}=21.8$.

$\text{C}_5\text{H}_6\text{O}_2\text{N}_2\cdot\text{HCl}$ requires $\text{C}=36.9$; $\text{H}=4.4$; $\text{Cl}=21.8$ per cent.

The *picrate* crystallises from hot water in handsome yellow plates, which melt at $212\text{--}213^\circ$ (corr.). It is anhydrous and easily soluble in hot water or alcohol, but sparingly so in these solvents when cold:

0.1515 gave 0.2044 CO_2 and 0.0371 H_2O . $\text{C}=36.8$; $\text{H}=2.7$.

0.0830 „ 13.5 c.c. N_2 at 13° and 773 mm. $\text{N}=19.7$.

$\text{C}_5\text{H}_6\text{O}_2\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{C}=37.2$; $\text{H}=2.6$; $\text{N}=19.8$ per cent.

Sodium glyoxaline-4(or 5)-acetate crystallises from absolute alcohol in small needles containing half a molecular proportion of water of crystallisation, which is retained at 100° , but lost at 120° . This salt is very easily soluble in water, and fairly easily so in hot absolute alcohol:

0.1633 * lost 0.0087 at 120° . $\text{H}_2\text{O}=5.3$.

0.2144 * gave 0.0955 Na_2SO_4 . $\text{Na}=14.4$.

$\text{C}_5\text{H}_5\text{O}_2\text{N}_2\text{Na}\cdot\frac{1}{2}\text{H}_2\text{O}$ requires $\text{Na}=14.6$; $\text{H}_2\text{O}=5.8$ per cent.

0.1546 † gave 0.0724 Na_2SO_4 . $\text{Na}=15.2$.

$\text{C}_5\text{H}_5\text{O}_2\text{N}_2\text{Na}$ requires $\text{Na}=15.5$ per cent.

Ethyl Glyoxaline-4(or 5)-acetate, $\text{C}_3\text{H}_3\text{N}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$.

Five grams of 4(or 5)-cyanomethylglyoxaline were dissolved in 25 c.c. of absolute alcohol, and a stream of dry hydrogen chloride passed through the solution while boiling gently. After two or three minutes, ammonium chloride began to separate out, and after ten minutes, this was removed by filtration. The liquor was evaporated almost to dryness under diminished pressure, and the sticky residue dissolved in about 30 c.c. of hot acetone, when, on cooling, crude ethyl glyoxaline-4(or 5)-acetate hydrochloride separated. After recrystallisation from acetone, 4.2 grams of this salt were obtained in a pure state, and the mother liquors contained more of this salt mixed with glyoxaline-4(or 5)-acetic acid hydrochloride.

Ethyl glyoxaline-4(or 5)-acetate hydrochloride crystallises from acetone in clusters of prismatic needles, which melt at $115\text{--}117^\circ$ (corr.). It is deliquescent, very easily soluble in water or alcohol, fairly easily soluble in hot, but sparingly so in cold, acetone:

0.1538 * gave 0.2471 CO_2 and 0.0803 H_2O . $\text{C}=43.8$; $\text{H}=5.9$.

$\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2\cdot\text{HCl}$ requires $\text{C}=44.1$; $\text{H}=5.8$ per cent.

The free base may be isolated as a colourless oil by mixing the

* Dried at 100° .

† Dried at 120° .

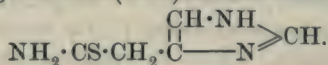
hydrochloride with a slight excess of 10 per cent. aqueous sodium carbonate, evaporating to dryness in a vacuum, and extracting with ethyl acetate.

The *hydrogen oxalate* crystallises from water in large prisms, which melt and decompose at 180° (corr.), after sintering a few degrees earlier. It is anhydrous, and is easily soluble in water, but sparingly so in alcohol:

0.1503 gave 0.2443 CO_2 and 0.0665 H_2O . $\text{C}=44.3$; $\text{H}=5.0$.

$\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2\cdot\text{C}_2\text{H}_2\text{O}_4$ requires $\text{C}=44.2$; $\text{H}=5.0$ per cent.

Glyoxaline-4(or 5)-acet-thioamide,



Three grams of 4(or 5)-cyanomethylglyoxaline were dissolved in 30 c.c. of alcohol, mixed with 30 c.c. of a cold saturated alcoholic solution of ammonium sulphide, and kept overnight at 40° in a closed vessel. On distilling off the greater part of the alcohol under diminished pressure, the thio-derivative crystallised from the residual liquor while still warm, and 2.5 grams of the pure substance in the form of a nearly white, crystalline powder were obtained in the first crop, and further small quantities subsequently.

Glyoxaline-4(or 5)-acet-thioamide crystallises well from water in prisms, and from absolute alcohol in rosettes of needles. On heating, it darkens slightly from about 140° , and considerably from 160° , and eventually melts and decomposes at 173° (corr.). It is easily soluble in hot water, fairly easily so in hot absolute alcohol, and sparingly so in these solvents when cold. It is anhydrous:

0.1543 gave 0.2419 CO_2 and 0.0703 H_2O . $\text{C}=42.8$; $\text{H}=5.1$.

$\text{C}_5\text{H}_7\text{N}_3\text{S}$ requires $\text{C}=42.5$; $\text{H}=5.0$ per cent.

On reducing 1 gram of this base with zinc dust and dilute hydrochloric acid in cold alcoholic solution for several days, and working up the reaction product for 4(or 5)- β -aminoethylglyoxaline, only about 0.05 gram of the dipicrate of this base was obtained.

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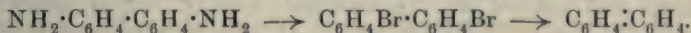
LXXV.—*Diphenylene. A New Aromatic Hydrocarbon.* *Part I.*

By JAMES JOHNSTON DOBBIE, JOHN JACOB FOX, and
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Two ways have long been known in which two benzene rings unite directly with one another. In the one the rings are united by one carbon atom of each ring, as in diphenyl. In the other the union is effected by means of two carbon atoms common to both rings, as in naphthalene and phenanthrene. So far, however, no hydrocarbon has been described in which two benzene rings are directly united by the linking of two carbon atoms of one ring to two carbon atoms of another. The present communication contains an account of the preparation of *diphenylene*, $C_6H_4:C_6H_4$:



a hydrocarbon of this type which we have prepared from 2:2'-diaminodiphenyl in accordance with the following scheme:



Niementowski (*Ber.*, 1901, **36**, 3331) attempted to prepare diphenylene by the action of copper powder on the diazonium salt of 2:2'-diaminodiphenyl; but instead of the expected hydrocarbon, he obtained carbazole. The action of sodium on *o*-dibromobenzene appears an obvious method for the preparation of diphenylene. This reaction was studied by Hosaeus (*Monatsh.*, 1893, **14**, 323), who, however, obtained a mixture of complex products due to the linking up of a number of benzene nuclei. Having satisfied ourselves by a repetition of Hosaeus's work that no diphenylene is produced in this way, we next turned our attention to the action of sodium on 2:2'-dibromodiphenyl. This derivative of diphenyl had not formerly been prepared, and we succeeded only after considerable difficulty in obtaining it from 2:2'-diaminodiphenyl. When heated with sodium in ethereal solution it yielded diphenylene in almost theoretical amount.

The new hydrocarbon melts at 74.5–75°, and possesses an odour very similar to that of diphenyl, from which, however, it is distinguished by its higher melting point. It is readily soluble in all the usual organic solvents, and is volatile in steam. It crystallises from its solution in light petroleum in prisms which appear colourless when thin, but show a distinct straw colour when from 1 to 2 mm. thick. It yields an absorption spectrum which differs from

that of diphenyl in the position of the limits of absorption. With layers 100 mm. thick of solutions of diphenylene and diphenyl of the strength of $N/100$, the absorption begins at $1/\lambda$ 2968 in the case of the former and at $1/\lambda$ 3195 in that of the latter.

The constitution of the hydrocarbon follows from its mode of preparation and from the fact that it yields phthalic acid when oxidised with chromic acid mixture.

It appeared possible that the action of sodium on 2:2'-dibromodiphenyl might result in the formation of tetraphenylene, $C_{24}H_{16}$, or of a dibromo-derivative, $C_{24}H_{16}Br_2$, but no such substances were obtained. Molecular-weight determinations showed clearly that the new hydrocarbon possesses the formula $C_{12}H_8$.

EXPERIMENTAL.

A solution of 2:2'-dibromodiphenyl (melting at 81°) in ether, which had been recently dried over sodium, was boiled with sodium under a reflux condenser. The reaction proceeded very slowly, and the heating was continued as long as freshly cut sodium was seen to be attacked.

When the ether was decanted from the sodium and sodium bromide and distilled off, the remaining syrupy, faintly yellow and slightly fluorescent liquid set almost at once to a mass of crystals. These were dissolved in light petroleum (b. p. below 60°), the solution filtered, and kept until crystals deposited. The first and second crops of crystals were united, and again crystallised from light petroleum and afterwards from alcohol. After several recrystallisations, the crystals were obtained in prisms melting at $74.5-75^\circ$.

The only other product of the reaction was a trace of a brown substance, which was insoluble in ether.

The substance obtained in the manner above described proved difficult to analyse on account of its extreme volatility. Concordant results were finally obtained by using tubes containing rather more than two feet of copper oxide, of which the greater part was maintained at a high temperature. The second analysis was conducted in a bayonet tube:

0.1432 gave 0.4954 CO_2 and 0.0722 H_2O . C=94.37; H=5.64.

0.1190 „ 0.4120 CO_2 „ 0.0606 H_2O . C=94.42; H=5.66.

0.1230 „ 0.4271 CO_2 „ 0.0561 H_2O . C=94.70; H=5.11.

Mean C=94.50; H=5.44.

$C_{12}H_8$ requires C=94.67; H=5.33 per cent.

Two determinations of the molecular weight were made, acetone being selected as the solvent on account of its non-associating

properties. The specimens used for these determinations were from different preparations:

(1) 0.1125 in 19.75 acetone gave $E = 0.056^\circ$. M.W. = 169.

(2) 0.2037 „ 18.40 „ „ „ $E = 0.113^\circ$. M.W. = 164.

$C_{12}H_8$ requires M.W. = 152.

Although these results are a little high, they leave no doubt that the formula of the substance is $C_{12}H_8$, and not $C_{24}H_{16}$, which has the molecular weight 304.

Diphenylene is not attacked by cold alkaline solutions of permanganate, and only slightly by boiling permanganate. In the latter case, so far as there is any action, complete oxidation seems to result. When boiled for several hours with chromic acid mixture, the hydrocarbon is partly oxidised to carbon dioxide, and partly to a mixture of phthalic and benzoic acids, the separation of which was effected by means of chloroform in the usual way. The production of benzoic acid may perhaps be explained by the rupture of the middle four-membered ring, which is probably in a condition of considerable strain.

It is a remarkable circumstance that commercial diphenyl, which closely resembles diphenylene, gives on oxidation a small quantity of phthalic acid as well as benzoic acid—the main product of the oxidation. This is probably due to the presence of a small quantity of diphenylene. In any case we have proved that diphenyl prepared by the action of sodium on bromobenzene gives no phthalic acid on oxidation if it has been separated from the products of the reaction by distillation in steam. If, however, it has been distilled at a high temperature, a distinct reaction for phthalic acid is obtained.

We propose in a future communication to give an account of some of the derivatives of diphenylene, and to describe more particularly the preparation and properties of 2:2'-dibromodiphenyl.

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LXXVI.—*Molecular Association in Water.*

By CYRIL JAMES PEDDLE and WILLIAM ERNEST STEPHEN TURNER.

SOLUTION in water has usually been regarded as a process accompanied by a simplification of the molecular complexity of the material dissolved. The fact that normal molecular weights in dilute aqueous solution are found for substances, such as acetic acid

or sucrose, which are either known or may be conjectured to be associated, is generally ascribed to the dissociating power of water. Further, the deviations from the normal observed in aqueous solutions of electrolytes have been interpreted in such a manner as to accentuate this view of the dissociating power of this solvent, a mode of explanation which apparently takes no account of the initial associated character of the solute, and considers, for the purpose, that the original molecules exist as single units.

There is another type of abnormal result known, and here, again, depressions of the freezing point greater than calculated are found, as with concentrated solutions of glycerol, sucrose, dextrose, ethyl alcohol, etc. (Abegg, *Zeitsch. physikal. Chem.*, 1894, **15**, 209), results which have more recently received an explanation on the theory of hydrate formation (Jones and Getman, *Amer. Chem. J.*, 1904, **32**, 308).

In both these types of abnormal result, then, the molecular weights observed are always less than the calculated values, a general experience which has engendered a disinclination to expect association in water. Moreover, according to the Nernst-Thomson hypothesis, molecular association in solution should be expected to diminish as the dielectric constant of the solvent increases; the dielectric constant of water is also very high.

The observation by Dr. A. N. Meldrum that benzamide is associated in aqueous solution, led to the series of papers by Meldrum and Turner on the molecular complexity of amides in various solvents (Trans., 1908, **93**, 876; 1910, **97**, 1605, 1805), and resulted in proving that many other amides and anilides are associated in water. This is an important matter in connexion with the Nernst-Thomson hypothesis, which Dr. Meldrum had specially in view when the work began. The present communication, which deals with the behaviour in aqueous solution of certain carboxylic acids, phenols, and amines, affords ample confirmation of the results already obtained with the amides.

As a matter of fact, one or two cases of abnormally high molecular weight in aqueous solution have been noticed by other workers. Thus, Abegg (*loc. cit.*) found that in concentrated solutions of acetic and propionic acids, the molecular depressions of the freezing point of water decreased as the concentration of acid increased; and, later, Loomis (*Zeitsch. physikal. Chem.*, 1901, **37**, 407) stated that from results with seven substances, including aniline, benzamide, phenol, catechol, and resorcinol, he concluded that benzene compounds exist in aqueous solution in the form of molecular aggregates, the association increasing with concentration. Except in the case of aniline, Loomis has not given data in support of his conclu-

sion, and we were unaware even of the statement until our work was nearly completed.

The determination of molecular weights in water, at any rate of such substances as it was thought desirable to examine in connexion with this paper, is attended with certain difficulties. Two distinct regularities are noticeable. We find, for example, that the substances which are most soluble in benzene and least soluble in water are, on the whole, just those which have abnormally high molecular weights in water; and surely this is the reason for the late discovery of molecular association in water, that the substances used hitherto are those readily soluble in this solvent. Exemplification is found in the highly associated, but little soluble, benzoic and salicylic acids, as compared with acetic and mandelic acids, which are readily soluble, and not associated in water. Contrast also phenol and *p*-nitrophenol. A still better example is afforded by phloroglucinol, which is more associated and less soluble in water than pyrogallol. The toluic acids, which may reasonably be expected to behave like benzoic acid, were not sufficiently soluble in water to permit examination.

Not only are the most associated substances the least soluble, but they are also those most liable to distil over in steam. A notable instance of this occurs with methylacetanilide (Meldrum and Turner, *loc. cit.*), and distinct examples occurring in the present investigation are benzoic and phenylacetic acids, phenol, and aniline. Guaiacol, thymol, and *o*-nitrophenol were both too sparingly soluble and too easily volatile in steam to be used. In an experiment carried out in the Beckmann boiling-point apparatus, guaiacol was found actually to lower the boiling point of water.

In addition to the determinations in water, experiments in benzene solution have also been carried out wherever the solubilities allowed. Such determinations were made for the purpose of establishing the views expressed on the nature of the apparent association in water, and any comments on the results are made with this end in view. A few results have been obtained from the numbers published by other workers, and references are quoted in the text.

EXPERIMENTAL.

The materials used were obtained mainly from Kahlbaum, some from Schuchardt, and were all subjected to careful purification: phenol, propionic and butyric acids and the amines by distillation, either under the atmospheric or diminished pressure, the other materials by crystallisation, water or benzene being used almost exclusively for the purpose.

For the most part, the measurements have been carried out at the boiling point, one of them, *m*-nitroaniline, in water, by the Beckmann process, the others by the method previously described by one of us (Turner, Trans., 1910, **97**, 1184). Freezing-point measurements have been made with propionic and butyric acids, the amines, and with phenol. The range of concentration over which experiments have been made at the boiling point is, in a number of cases, somewhat limited. The low molecular boiling-point elevation of water prevents the accurate investigation of weak solutions, and, as already mentioned, the sparing solubilities of some of the solutes narrows the range. Our main object has been, however, to carry out the measurements at, or about, a certain suitable concentration, at which the molecular complexity of the different substances could be compared.

There are three cases—those of benzoic, salicylic, and phenylacetic acids—in which a special treatment was adopted. Benzoic acid is distinctly volatile in steam. In Watts's *Dictionary of Chemistry* it is stated that the amount distilling over is 1 gram in 2000 c.c. of water. We have made a number of experiments on this point by passing steam through a solution of known concentration, namely, 6—7 per cent. at the boiling point. The solution was placed in the molecular-weight apparatus, steam blown in, and the residual benzoic acid determined by titration with barium hydroxide solution. By this means we found, in three separate experiments, losses of 4.7, 4.6, and 5.06 grams per 1000 c.c. of water distilled. Since the quantity of water passing over during a molecular-weight determination is but small, 10—20 c.c. at most, the loss of material is small. We have avoided this source of error, however, by employing the formula applicable to volatile substances (Beckmann and Stock, *Zeitsch. physikal. Chem.*, 1895, **17**, 107), namely,

$$M = \frac{C(1 - \alpha)K}{\Delta},$$

where *C* is the concentration of the solution in grams of substance per 100 grams of solvent, *α* is the ratio of the concentration of the substance in the vapour to that in the solution, and *K* is the molecular elevation of boiling point calculated for 100 grams of solvent. The values necessary for the calculation were obtained during the molecular-weight determination by titrating the acid carried over by the steam.

Salicylic acid and phenylacetic acid are appreciably volatile, and their molecular weights have been calculated by this same formula. The most volatile substance, benzoic acid, is the one which is most associated in water; and phenylacetic, the least volatile, is also least

associated. The differences between the molecular weights calculated by the ordinary formula and by the modified formula are not very great.

In calculating the results, we have used the following constants for the molecular depression or elevation:

	F. pt.	B. pt.
Water	1860	510
Benzene	5000	2610
Alcohol.....	—	1170

and the results of other authors quoted in our tables have been recalculated to these standards.

Control experiments have been made throughout with the aqueous solutions, but are not recorded.

In the tables, the symbols w , W , and Δ signify the weight of solute, the weight of solvent, and the rise of boiling point respectively.

C =concentration of the solution at the moment when the boiling temperature was recorded.

C_g =concentration of the substance in the vapour, in grams per 100 grams of solvent.

It should be noted that the values of C_g are fairly constant, whereas the values of α increase as the solution becomes more dilute. The behaviour is, therefore, different from that of iodine dissolved in chloroform, benzene, etc., where C_g varies and α is constant (Beckmann and Stock, *loc. cit.*; Beckmann, *Zeitsch. physikal. Chem.*, 1907, **58**, 543).

N =number of milligram-molecules per 100 c.c. of pure solvent, water, or benzene, as the case may be.

The specific gravities used in calculating these values were, for water at the boiling point, 0.9587; for benzene, at the boiling point, 0.8149 (Beckmann, *Zeitsch. physikal. Chem.*, 1890, **6**, 437), and at the freezing point, 0.888 (Lachowicz, *Ber.*, 1888, **21**, 2210); for alcohol, at the boiling point, 0.7389 (Beckmann, *loc. cit.*).

Solvent—Water.

Experiments at the Boiling Point.

Benzoic Acid (M. W. = 122).

C .	C_g .	α .	$(1 - \alpha)$.	Δ° .	N .	M. W.
7.288	0.460	0.0631	0.9369	0.140	57.3	249
7.141	0.460	0.0644	0.9356	0.132	56.1	258
6.813	0.470	0.0690	0.9310	0.130	53.5	249
6.088	0.506	0.0831	0.9169	0.121	47.8	235

Salicylic Acid (M. W. = 138).

C .	C_g .	α .	$(1 - \alpha)$.	Δ° .	N .	M. W.
7.436	0.346	0.0454	0.9546	0.152	51.7	238
5.980	0.325	0.0544	0.9456	0.137	41.5	206
4.873	0.311	0.0639	0.9361	0.125	33.8	186
3.966	0.282	0.0711	0.9289	0.106	27.5	177

Phenylacetic Acid (M.W. = 136).

<i>C.</i>	<i>C_g.</i>	<i>a.</i>	(1 - <i>a</i>).	Δ° .	<i>N.</i>	M.W.
9.124	0.269	0.0295	0.9705	0.201	64.3	225
7.288	0.249	0.0342	0.9658	0.180	51.4	199
5.927	0.268	0.0453	0.9547	0.152	41.8	190
5.038	0.261	0.0517	0.9483	0.134	35.5	183

Oxalic Acid (M.W. = 90).

2.168 grams.

<i>W</i> (grams).	Δ° .	<i>N.</i>	M.W.
22.41	0.660	103.1	74.7
25.61	0.578	90.2	74.7
36.23	0.408	63.8	74.8
46.13	0.333	50.1	72.1

Succinic Acid (M.W. = 118).

2.000 grams.

<i>W</i> (grams).	Δ° .	<i>N.</i>	M.W.
26.34	0.322	61.0	118.9
31.12	0.273	51.6	118.7
37.04	0.226	43.4	120.5
41.52	0.204	38.7	119.1
44.56	0.184	36.0	123.0

m-Hydroxybenzoic Acid, (M.W. = 138).

2.289 grams.

28.66	0.233	55.4	175
32.43	0.212	49.0	170
39.86	0.176	39.8	166
42.09	0.161	37.6	172
47.06	0.158	33.8	157

p-Hydroxybenzoic Acid (M.W. = 138).

2.321 grams.

32.08	0.235	50.3	157
40.15	0.194	40.2	152
43.78	0.182	36.7	147
47.86	0.172	33.8	144
53.75	0.156	30.0	141

Phthalic Acid (M.W. = 166).

2.786 grams.

30.72	0.341	52.4	136
34.42	0.314	46.7	131
40.30	0.268	39.9	131
47.55	0.231	33.8	129

Mandelic Acid (M.W. = 152).

2.038 grams.

29.50	0.221	42.7	157
32.00	0.205	39.4	155
34.60	0.185	36.4	159
39.67	0.165	31.8	156

Protocatechnic Acid (M.W. = 154).

2.241 grams.

19.56	0.302	71.3	193
25.23	0.241	55.3	188
31.86	0.188	43.8	191
40.33	0.151	34.6	188

p-Nitrophenol (M.W. = 139).

1.621 grams.

28.73	0.147	38.9	196
31.68	0.136	35.2	192
36.93	0.119	30.3	188

Catechol (M.W. = 110).

1.200 grams.

23.00	0.209	47.4	127.4
26.03	0.185	41.9	126.8
31.55	0.157	34.6	123.9
36.55	0.133	29.8	126.0

0.973 grams.

31.19	0.090	21.5	177
38.33	0.079	17.5	164
44.18	0.072	15.1	156

Resorcinol (M.W. = 110).

21.12	0.298	60.9	119.6
28.49	0.221	45.1	119.3
36.77	0.175	35.8	117.0

1.199 grams.

30.00	0.170	36.3	119.9
36.49	0.140	29.9	119.7

Pyrogallol (M.W. = 126).

2.231 grams.

17.44	0.458	97.3	142
23.97	0.344	70.8	138
30.77	0.268	55.2	138
40.27	0.203	42.1	139

Quinol (M.W. = 110).

31.10	0.256	50.2	115.0
40.25	0.197	38.9	115.5
45.73	0.174	34.2	115.1
54.87	0.145	28.5	115.1

Phloroglucinol (M.W. = 126).

2.024 grams.

18.43	0.360	83.5	156
27.00	0.246	57.0	155
35.36	0.180	43.5	162
43.66	0.141	35.3	168

m-Nitroaniline (M.W. = 138).

Solvent: 16.97 grams.

<i>w</i> (grams).	Δ° .	<i>N.</i>	M.W.
0.2944	0.050	12.0	177
0.3654	0.063	15.0	174

Experiments at the Freezing Point.

Propionic Acid (M. W. = 74.05).

Solvent: 11.09 grams.

<i>w</i> (grams).	Δ° .	<i>N</i> .	M. W.
0.0912	0.229	11.1	66.8
0.1502	0.356	18.3	70.9
0.1727	0.407	21.0	71.2
0.3230	0.737	39.3	73.5
0.5195	1.160	63.4	75.1
0.7934	1.705	96.6	78.0
1.7156	3.393	208.9	84.8

Butyric Acid (M. W. = 88.06).

Solvent: 10.90 grams.

<i>w</i> (grams).	Δ° .	<i>N</i> .	M. W.
0.1686	0.352	17.6	81.7
0.2796	0.550	29.1	86.7
0.3597	0.687	37.5	89.3
0.4406	0.829	45.9	90.7
0.5724	1.049	59.6	93.1
0.6644	1.199	69.2	94.6
1.0473	1.804	109.1	99.1

Phenol (M. W. = 94).

Solvent: 9.09 grams.

0.1014	0.215	11.8	96.5
0.2023	0.429	23.8	96.5
0.3159	0.627	37.0	103.1
0.4292	0.827	50.2	106.2
0.4687	0.897	54.8	106.9

Propylamine (M. W. = 59.1).

Solvent: 10.90 grams.

0.2538	0.767	39.4	56.5
0.4530	1.321	70.3	58.5
0.5050	1.467	78.4	58.7

Solvent: 14.82 grams.

0.5050	1.152	57.7	55.0
0.7629	1.519	87.1	63.0

isoAmylamine (M. W. = 87.1).

Solvent: 10.91 grams.

0.1005	0.203	10.6	84.8
0.1831	0.359	19.3	87.0
0.3223	0.632	33.9	87.1
0.4300	0.838	45.3	87.5
0.5476	1.069	57.7	87.3
0.7760	1.500	81.8	88.2

Benzylamine (M. W. = 107.1).

Solvent: 11.40 grams.

0.1512	0.258	13.7	105.5
0.2666	0.413	24.0	115.4
0.3622	0.553	32.5	117.1
0.4834	0.708	43.4	122.1
0.6282	0.836	56.4	134.4

Ethylamine (M. W. = 45.07).

Solvent: 17.02 grams.

0.4033	1.008	52.6	43.7
0.6919	1.603	90.2	47.1

Solvent: 10.30 grams.

0.4033	1.592	86.9	45.7
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Solvent: 12.36 grams.

0.9236	2.971	165.8	46.8
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Dipropylamine (M. W. = 101.1).

Solvent: 10.30 grams.

0.3015	0.536	18.3	101.3
0.3634	0.634	34.9	103.4
0.4570	0.787	43.9	104.6
0.6022	1.040	57.9	104.3
0.8338	1.428	80.1	105.2

Aniline (M. W. = 93.1).

Solvent: 10.57 grams.

0.2089	0.367	21.2	100.2
0.2719	0.467	27.6	102.5
0.4114	0.674	41.8	107.4

Solvent: 14.30 grams.

0.5071	0.633	38.1	104.2
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Solvent: 15.97 grams.

0.6501	0.703	43.7	107.7
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*Solvent—Benzene.**Experiments at the Boiling Point.**Phenylacetic Acid* (M. = 136).

1.525 grams.

<i>W</i> (grams).	Δ° .	<i>N</i> .	M. W.
17.45	0.988	52.4	231
24.80	0.722	36.8	222
33.58	0.547	27.2	217
42.88	0.443	21.3	209

Mandelic Acid (M. W. = 152).

1.019 grams.

<i>W</i> (grams).	Δ° .	<i>N</i> .	M. W.
25.08	0.408	21.8	260
36.68	0.317	14.9	229
45.03	0.283	12.1	209

0.811 gram.

20.86	0.378	20.8	268
31.46	0.298	13.8	226
39.31	0.264	11.1	204

p-Nitrophenol (M. W. = 139).

1.478 grams.

20.72	0.961	51.3	194
29.14	0.759	36.5	174
38.67	0.623	27.5	160
48.44	0.527	21.9	151

m-Nitroaniline (M. W. = 138).

1.253 grams.

17.30	1.151	42.8	164
26.15	0.809	28.3	155
39.23	0.566	18.9	147
47.95	0.486	15.4	140

Catechol (M. W. = 110).

1.373 grams.

20.68	1.267	49.2	137
28.78	0.977	35.3	127
37.38	0.793	27.2	121
44.50	0.675	22.9	119

Resorcinol (M. W. = 110).

0.800 gram.

21.60	0.713	27.4	136
30.40	0.562	19.5	122
37.30	0.472	15.9	117
45.70	0.399	13.0	114

*Experiments at the Freezing Point.**Propionic Acid* (M. W. = 74.05).

Solvent: 9.02 grams.

<i>w</i> (grams).	Δ° .	<i>N</i> .	M. W.
0.1188	0.471	15.8	139.8
0.3110	1.201	41.4	143.5
0.4988	1.890	66.4	146.3
0.7114	2.665	94.6	148.0
1.0302	3.770	137.1	151.5
1.1567	4.222	153.9	151.9

Butyric Acid (M. W. = 88.06).

Solvent: 9.83 grams.

<i>w</i> (grams).	Δ° .	<i>N</i> .	M. W.
0.0935	0.303	9.60	157.0
0.2140	0.684	22.0	159.2
0.4841	1.473	49.7	166.6
0.6573	1.971	67.5	167.1
0.9887	2.903	101.5	173.3
1.1013	3.206	113.0	174.6

Ethylamine (M. W. = 45.07).

Solvent: 9.47 grams.

0.1510	1.380	31.3	57.4
0.2957	2.734	61.6	57.1
0.4224	3.830	88.0	58.2

Aniline (M. W. = 93.1).

Solvent: 8.75 grams.

0.1600	0.875	17.4	104.5
0.3140	1.622	34.2	110.6
0.5492	2.670	59.9	117.5
0.7726	3.631	84.2	121.5

Solvent: 13.42 grams.

0.7194	4.520	105.8	59.3
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Discussion of Results.

The only class of substance in which no association is evident is that of the aliphatic amines, a fact to be accounted for, probably, by a chemical combination with the water to such an extent as to counterbalance or to mask any apparent association. With the two aromatic amines, chemical combination of amine and water

does not predominate, and aniline and benzylamine are distinctly associated in water. We are thus able to confirm the statement of Loomis regarding the behaviour of aniline. In the case of benzylamine, which we have tested at still higher concentrations than those recorded, the molecular weight continues to increase with concentration. We have observed, however, that the crystals which separate on freezing appear to be different from ice crystals, and further examination is accordingly required to test whether this amine freezes out with the water.

One fact emphasised by the behaviour of aniline and by the other substances examined, is that the aromatic compounds exhibit the phenomenon of association in water to a greater extent than the aliphatic.

Regarding now our results as a whole, it is clear that molecular association in water is of very frequent occurrence. Out of twenty-eight substances examined (including formic and acetic acids), sixteen, namely, butyric, benzoic, salicylic, *m*-hydroxybenzoic, *p*-hydroxybenzoic, phenylacetic and protocatechuic acids, phenol and *p*-nitrophenol, catechol, resorcinol, phloroglucinol, pyrogallol, benzylamine, aniline, and *m*-nitroaniline, are distinctly, in some of these cases strongly, associated in dilute aqueous solution, and a number of other substances show unmistakable evidence of a tendency to association. The aliphatic acids do not show any marked tendency to association until the solutions become concentrated, but, just as in the case of the aliphatic amines, the association in water increases with the molecular weight of the acid. It is possible that separation of the aliphatic acids with water in the form of mixed crystals or compounds may account for the higher molecular weights obtained (Balló, *Zeitsch. physikal. Chem.*, 1910, **72**, 439), but this explanation does not appear to us to satisfactorily account for the fact that formic and acetic acids are only very slightly associated, or for the gradual increase of association with increase of molecular weight of the acid.

The dicarboxylic acids do not show evidence of association. On the contrary, oxalic and phthalic acids are distinctly dissociated. Oxalic acid is a fairly strong acid, and we should accordingly look for marked evidence of dissociation. The strong acids dichloroacetic (Hausrath, *Ann. Physik*, 1892, [iv], **9**, 348; Peterson, *Zeitsch. physikal. Chem.*, 1893, **11**, 183), and trichloroacetic (Wildermann, *Zeitsch. physikal. Chem.*, 1894, **15**, 349), give abnormally low molecular weights in aqueous solution. If we seek for further connexion between the strength of the acid, as usually measured by the dissociation constant, and the tendency to dissociate or associate in water, we are disappointed; there appears to be no

direct connexion. To make only a selection, the following values of the affinity constants, compared with the degree of association (A) at a concentration of 50 milligram-molecules per 100 c.c. of pure solvent, indicate the absence of parallelism between the two properties.

Acid.	K (100 k).	A .
Oxalic	10.0	0.80
Phthalic	0.121	0.81
Salicylic	0.102	1.70
Benzoic.....	0.0060	1.98
Phenylacetic	0.00502	1.46
Butyric.....	0.00015	1.05

The case of benzoic acid is interesting. In common with a number of carboxylic acids, it has a molecular weight in benzene, even in dilute solution, approaching twice the formula weight. In water, the molecular weight of the acid is as great as in benzene.

Whilst a connexion between the strength of an acid and its tendency to association cannot be established, we do find that, as with the amides in aqueous solution (Meldrum and Turner, *loc. cit.*), the more highly associated the substance is in the free state or in benzene solution, the less is it associated in water. In order to establish this fact, we have tabulated on p. 695 the molecular weights in water, and, as far as possible, in benzene, at a concentration of 50 milligram-molecules per 100 c.c. of solvent; the degree of association (A) at this concentration, and also the degree of association (α) of the substance in the fused state, where measurements have been made. Catechol and resorcinol, and phenylacetic and mandelic acids have been compared in the second section of the table, at a concentration of 30 milligram-molecules, owing to the sparing solubility of resorcinol and mandelic acid in benzene.

The comparison is not as complete as we could desire, owing to the fact that the substances readily soluble in water are generally but sparingly soluble in benzene and similar solvents. Comparison can be made between the members of the following groups: formic, acetic, propionic and butyric acids; the *o*-, *m*-, and *p*-hydroxybenzoic acids; phenylacetic and mandelic acids; phenol and *p*-nitrophenol; and the di- and tri-hydroxyphenols. As direct evidence of the extent of association in benzene is either lacking or is incomplete in two of these groups, namely, in the hydroxybenzoic acids and dihydroxyphenols, some explanation is needed. In the case of the dihydroxyphenols, we attempted a direct comparison of the extent of association in the fused state, but the viscosity of catechol to some extent, and more particularly of resorcinol, even up to a temperature 50° above the melting point, rendered the measurements useless. Where direct evidence is wanting, however, there is other evidence to prove that molecular association in benzene

		In Water.		In Benzene.		Liquid State.
		M.W.	A.	M.W.	A.	α .
Acids.	Formic.....	45.6	0.99	—	—	3.61 ¹
	Acetic	60.6	1.01	122.0	2.03 ⁴	3.62 ¹
	Propionic.....	74.5	1.01	144.5	1.95	1.77 ¹
	<i>n</i> -Butyric	92.0	1.05	167.1	1.90	1.58 ¹
	Oxalic	72.1	0.80	—	—	—
	Succinic	119.0	1.01	—	—	—
	Benzoic	241.0	1.98	240.0	1.97 ⁵	—
	Salicylic	233.0	1.70	255.0	1.85 ⁵	—
	<i>m</i> -Hydroxybenzoic	170.0	1.23	—	—	—
	<i>p</i> -Hydroxybenzoic.....	157.0	1.14	—	—	—
	Phenylacetic	198.0	1.46	229.0	1.68	—
	Phthalic	135.0	0.81	—	—	—
	Protocatechuic	192.0	1.25	—	—	—
Phenols.	Phenol	106.2	1.13	178.0	1.89 ⁴	1.42 ¹
	<i>p</i> -Nitrophenol	202.0	1.46	192.0	1.38	1.25 ²
	Catechol	128.0	1.16	137.0	1.25	—
	Quinol	115.0	1.05	—	—	—
	Phloroglucinol	159.0	1.26	—	—	—
	Pyrogallol	138.0	1.09	—	—	—
Amines.	Ethylamine	43.6	0.97	57.0	1.29	—
	Propylamine	57.2	0.97	—	—	1.24 ³
	Dipropylamine	104.5	1.04	—	—	0.90 ³
	<i>iso</i> Amylamine	87.4	1.00	101.0	1.16 ³	1.13 ³
	Aniline	110.0	1.18	115.0	1.24	1.40 ³
	Catechol	126.0	1.14	124.0	1.13	—
	Resorcinol	119.0	1.08	140.0	1.27	—
	Phenylacetic acid	177.0	1.30	218.0	1.53	—
	Mandelic acid	156.0	1.08	317.0	2.07	—

¹ Ramsay and Shields (Trans. 1893, **63**, 1103; 1894, **65**, 168).

² Hewitt and Winmill (*ibid.*, 1907, **91**, 446).

³ Turner and Merry (*ibid.*, 1910, **97**, 2069).

⁴ Beckmann (*Zeitsch. physikal. Chem.*, 1888, **2**, 715).

⁵ Beckmann (*ibid.*, 1890, **6**, 440).

increases in the order *o*-, *m*-, *p*-hydroxybenzoic acid; and catechol, resorcinol, quinol. For Auwers (*Zeitsch. physikal. Chem.*, 1895, **18**, 619; 1896, **21**, 337) showed that in naphthalene solution the para-substituted phenols were always most associated, and the ortho-, least; the meta-substituted carboxylic acids more than the ortho-; the ester of *p*-hydroxybenzoic acid most associated, and that of the ortho-acid, least.

There is therefore clear evidence from a comparison of the five groups named that, as in the case of the amides, the more highly associated a substance is in benzene or in the fused state, the less is it associated in aqueous solution, and vice versa.

The type of molecular association in solution of which our results give evidence is similar to that observed earlier by Robertson (Trans., 1903, **83**, 1904; 1904, **85**, 1425, 1617; 1905, **87**, 1574; 1906, **89**, 567), who employed phenol as solvent. He found, for example, that a number of hydrocarbons and their halogen derivatives, all of them substances of normal molecular weight in

the free state or in benzene solution, were associated in phenol solution (*loc. cit.*, 1905, **87**, 1574). In keeping with these observations, we would draw attention to the fact that such solutes are also capable of association in ethyl alcohol. The measurements which we record below were made on substances which have been employed from time to time as normal solutes in the determination of molecular elevation of boiling point or depression of freezing point.

Solvent: Ethyl Alcohol.

Diphenylamine (M.W. = 169).
2.200 grams.

<i>W</i> (grams).	Δ° .	<i>N</i> .	M.W.
16.15	0.775	59.9	206
20.75	0.631	46.3	197
25.35	0.535	37.9	190

Benzil (M.W. = 210).
2.137 grams.

<i>W</i> (grams).	Δ° .	<i>N</i> .	M.W.
16.31	0.585	46.1	262
22.21	0.449	33.9	251
28.21	0.375	26.6	236
34.61	0.308	21.7	234

m-Dinitrobenzene (M.W. = 168).

<i>W</i> (grams).	Δ° .	<i>N</i> .	M.W.
17.52	0.672	55.3	211
22.80	0.552	40.9	197
29.79	0.449	31.3	186
35.89	0.382	26.0	181

Again, according to the measurements of Beckmann (*Zeitsch. physikal. Chem.*, 1890, **6**, 437), naphthalene, benzil, and ethyl benzoate are all distinctly associated in ethyl alcohol, although in benzene solution they possess the normal molecular weight.

So far as molecular-weight measurements can throw light on the phenomena occurring on solution, the abnormally small elevation of boiling point or depression of freezing point represents a diminution in the value of n/N , the ratio of the number of molecules of the solute to that of the solvent. Such a diminution may be due either to an increase in the value of N or to a decrease in the value of n . The first of these alternatives means dissociation of the more complex water molecules into simpler ones, a process involving a diminution in the concentration of the solution. Robertson (*loc. cit.*) was led to adopt this conclusion in the case of phenol, not only because of the association of so-called normal substances in phenol, but also because, when substituted phenols of diminishing molecular complexity were employed as solvents, the association of the hydrocarbons also diminished. Since in aqueous solution it has been shown that, when series of similar substances are compared, the substance is more associated in water the less the association in benzene, the conclusion is at least suggested that the explanation of the association may be traced to an actual dissociation of the

solvent. It is well known that complex molecular hydroxyl-containing substances, including water, are easily dissociated into simple molecules and in dilute solution in indifferent solvents the normal molecular weights are found (see Bruni and Amadori, *Gazzetta*, 1910, **40**, ii, 1). Again, from a measurement of the partial pressures of aqueous solutions of ether, Nernst (*Zeitsch. physikal. Chem.*, 1892, **8**, 136) concluded that in ether, water exists for the most part as single molecules. It may be noted that when, in turn, ether is dissolved in water, an abnormally small depression of freezing point is recorded (Loomis, *loc. cit.*). Such facts as these make quite credible the view that the process of dissolving certain substances in water is possibly accompanied by a simplification of the molecular structure of the solvent.

On the other hand, association in water may be no different in type from that ordinarily recognised, namely, an actual association of the solute itself. There are two considerable difficulties which this method of explanation must meet. Firstly, the substances which are, on the whole, most strongly associated in water and in alcohol are those which we least expect to behave in this way. Secondly, if marked association of the ordinary type occurs in water, then the Nernst-Thomson rule, that molecular association will occur to the greatest extent only in solvents of low dielectric constant, signally fails in connexion with water.

The problem resolves itself into the question whether, with the substances used here as solutes, the water forces the solute to associate, or the solute compels the water to undergo a change into a simpler molecular state. For the second alternative, we believe there is as much favourable evidence as for the first. Our results, at any rate, are explainable on the basis of this view.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which met most of the expense of this investigation.

THE GRAMMAR SCHOOL,
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THE UNIVERSITY,
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LXXVII.—*Physical Properties of Mixtures of Ether and Sulphuric Acid.*

By JAMES ROBERT POUND, B.Sc. (Victorian Government Research Scholar).

ADDITIVE compounds of ether and various salts have been long known, as well as similar compounds of ether and complex inorganic acids (Baeyer and Villiger, *Ber.*, 1901, **34**, 2679). Compounds of ether and the halogen hydrides were indicated by Friedel, and were isolated at low temperatures by Archibald and McIntosh (*Trans.*, 1904, **85**, 919), but with ether and sulphuric acid only syrupy mixtures were obtained, although with chlorosulphonic acid the compound $\text{HClSO}_3 \cdot 2\text{Et}_2\text{O}$ was separated (*J. Amer. Chem. Soc.*, 1905, **27**, 1013). Further, from the depression of the freezing point of "absolute sulphuric acid" by ether, Hantzsch assumes that diethylhydronium sulphate, $\text{Et}_2\text{O} \cdot \text{H}_2\text{SO}_4$, is present, and, in the dilute ethereal solutions used, mainly as Et_2OH^+ and HSO_4^- (*Zeitsch physikal. Chem.*, 1907, **61**, 257). Hence it was thought desirable to see what indication of complex formation in mixtures of ether and sulphuric acid would be given by a study of the physical properties of these solutions at the ordinary temperature.

In this investigation, two samples of sulphuric acid were employed. One was Schuchardt's ordinary concentrated acid. It was found to be of a high degree of purity, giving only the slightest residue on evaporation to dryness, and showing but the smallest trace of nitric acid. Its strength was found from the following data:

By titration with standard potassium hydroxide:	$\text{H}_2\text{SO}_4 = 94.9$	per cent.
By density at 20° ($= 1.8337$)	:	" = 95.1 "
By density at 30° ($= 1.8241$)	:	" = 95.25 "
Mean:	:	" = 95.1 "

Its specific conductivity at 30° was 0.1352 (mhos), and remained unaltered throughout the whole series of experiments, showing that the strength of the acid was constant for this period. We shall designate this acid as "95 per cent. acid."

The other acid used was "100 per cent. acid." This was made up from calculated amounts of the above "95 per cent. acid" and of fuming acid. The latter contained some sulphur dioxide, a little nitric acid, and 0.0016 gram of residue per 10 c.c. The residue was mostly iron oxide. The "100 per cent. acid" was slightly stronger than exact 100 per cent. (absolute) sulphuric acid, this being considered the safe side on which to err, as its strength decreases on keeping, through loss of sulphur trioxide, and by

absorption of water vapour. The course of such alteration in composition was followed throughout any series of experiments, chiefly by conductivity measurements, since this is the most delicate and the quickest method of determining the change in strength. The extreme variation in the specific conductivity of the "100 per cent. acid" at 30° was from 0.02518 to 0.02408. Taking Kohlrausch's results for the specific conductivities of concentrated sulphuric acids, the former value corresponds with acid containing 100.13 per cent. of H_2SO_4 , and the latter with 100.08 per cent., giving the mean strength of the acid as 100.1 per cent. of H_2SO_4 . The densities of different samples of the 100 per cent. acid were also taken from time to time at 30°, and varied from 1.8295 to 1.8292, the mean of five determinations over the whole period of use being 1.82935. This corresponds with acid of strength equivalent to 100.4 per cent. of H_2SO_4 , but this value may be high on account of the above impurities present in the fuming acid raising the density. Generally, the variations in the conductivity and in the density were parallel. The strength of the "100 per cent. acid" could not be very accurately determined by titration with alkali, owing to loss of sulphur dioxide, etc., while weighing out the acid; however, the mean strength of the acid was thus given as 100.3 per cent. H_2SO_4 . The "100 per cent. acid" is thus stronger than absolute sulphuric acid; it is probably 100.2 per cent. H_2SO_4 , but the maximum variation in strength, which is the more important, is not greater than 0.05 per cent.

Two samples of ether were used, of which the first was used with the "95 per cent. acid." This ether was shaken with sodium amalgam. The mercury in the amalgam decomposes the peroxides which are invariably present, whilst the sodium removes the alcohol and water in the ether. The ether was then distilled in small amounts as required from fresh amalgam, and was kept in the dark. This ether was not absolutely pure. It had, at 30°, a conductivity of about 1×10^{-6} , indicating the presence of traces of water, and, possibly, of alcohol. This is shown by its density, which is high; thus, at 20°, the density was 0.7139, and at 30°, 0.7026.

After the publication of Wade and Finnemore's paper on the purification of ether (*Trans.*, 1909, **95**, 1842), a more thorough purification was adopted for the second sample of ether, which was used with the "100 per cent. acid." This ether was washed with water, dried over calcium chloride for one month, and then over phosphoric oxide for a week. It was then distilled from phosphoric oxide, and kept over sodium amalgam in the dark. Wade and Finnemore mention no special treatment, save fractionation, for removing peroxides from ether. Small quantities of this stock of

ether were distilled as required from fresh amalgam. The density of this ether at 30° was 0.70200 (± 3). This is the mean value of several determinations, and is equivalent to that found by Wade and Finnemore for their best unfractionated ether. The conductivity of this ether was not measurable.

The mixtures of ether and sulphuric acid were prepared as follows. The sulphuric acid was weighed out in a well-stoppered bottle, the ether was added and mixed with the acid by shaking, the vessel being cooled under water as considerable heat is evolved on mixing, and, finally, the bottle with the mixture was weighed. The weights of acid and ether were not reduced to a vacuum, except for mixtures in table I. Absolute sulphuric acid and ether are apparently miscible in all proportions, but ether and dilute aqueous sulphuric acid, like ether and water, are not. Thus, with the "95 per cent. acid" and ether we could not get homogeneous solutions containing less than 10 per cent. of acid.

The experiments were mostly carried out at two temperatures, namely, 20° and 30°. These temperatures were maintained by the use of a thermostat which could be kept constant to within 0.01°. The thermometers used were compared with a standard. The physical properties examined were the density, specific conductivity, viscosity, surface tension, and vapour pressure. The results are discussed in this order; however, we may point out here that the work done with mixtures of the "100 per cent. acid" and of the purest ether is more accurate, and also more important, than that done with mixtures of the "95 per cent. acid" and of the less pure ether. Hence, excepting the vapour pressures, the former results alone are tabulated.

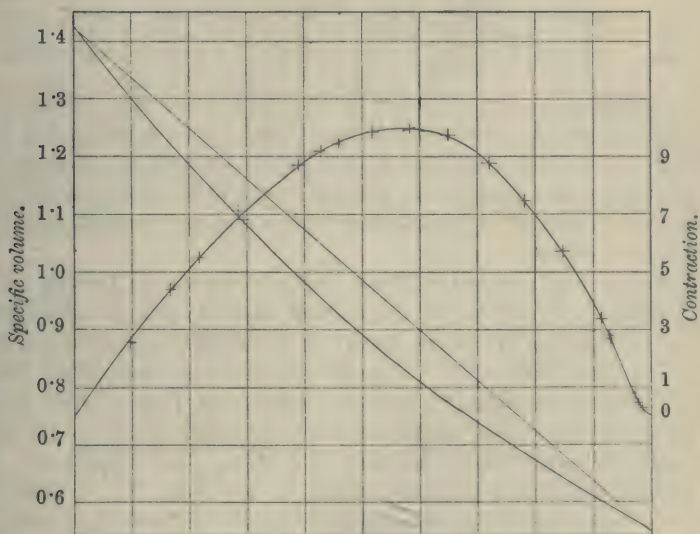
Density.

The densities of the solutions were found by means of the specific gravity bottle, used with all the ordinary precautions. With mixtures containing less than 40 per cent. of acid, bubbles are formed when the bottle filled with the mixture is immersed in the thermostat, especially when working at the higher temperature of 30°. If the ordinary form of specific gravity bottle with the capillary stopper were used, the experiment would thus be rendered useless, but by using a bottle with a wide, graduated, tubular stopper, the bubbles could be worked up the latter with a platinum wire, and the determination could be carried out. The same trouble occurs with pure ether, and is apparently due to dissolved air passing out of the liquid when it is raised to the higher temperature of the bath. Such minute bubbles of air grow larger owing to the high partial pressure of the ether vapour from the mixture at the temperature of the thermostat. Nevertheless, this bubble

formation was sometimes very troublesome, occasionally becoming continuous, and spoiling the experiment. Also, of the two duplicates carried out with a given mixture, one determination may proceed satisfactorily, whilst the other may be spoilt through bubbles—small impurities on the surface of the bottle may facilitate the evolution of bubbles. This bubble formation also occurs with the more ethereal mixtures in the determination of their viscosity and surface tension, but usually here it is not so troublesome.

The densities of mixtures of ether and "100 per cent. acid" are

FIG. 1.



given in table I, where the figure in the fifth decimal place is approximate. The specific volumes are also given in table I. All the densities are referred to that of water at 4° as unity, the density of water at 30° being taken as 0.995673.

In Fig. 1 the specific volume and the contraction on mixing are plotted against the percentage of acid in mixtures of ether and the "100 per cent. acid." The "contraction" given in table I is that occurring on mixing y c.c. of acid with $(100-y)$ c.c. of ether to form the mixture of the given percentage of acid.

TABLE I.

Mixtures of Ether and "100 per cent. acid."

Grams of acid in 100 grams of mixture.	Density ($^{30^{\circ}}$). ($^{4^{\circ}}$).	Specific volume ($^{30^{\circ}}$). ($^{4^{\circ}}$).	Contra- tion (c.c.).	Grams of acid in 100 grams of mixture.	Density ($^{30^{\circ}}$). ($^{4^{\circ}}$).	Specific volume ($^{30^{\circ}}$). ($^{4^{\circ}}$).	Contra- tion (c.c.).
100.000	1.82935	0.54664	0.00	58.312	1.21715	0.8216	9.97
98.683	1.79644	0.55666	0.275	52.111	1.14698	0.8718	9.845
98.002	1.78026	0.56172	0.44	46.175	1.08351	0.9229	9.44
97.392	1.76963	0.56509	0.78	43.010	1.05185	0.9507	9.19
93.171	1.69395	0.59034	2.68	39.125	1.01314	0.9870	8.70
92.955	1.69045	0.59156	2.785	29.601	0.92556	1.0854	6.80
91.536	1.66644	0.60009	3.36	28.523	0.91679	1.0908	7.10
84.843	1.56024	0.64093	5.705	21.779	0.85786	1.1657	5.48
78.065	1.46189	0.68405	7.46	16.777	0.81855	1.2217	4.35
72.016	1.38362	0.7227	8.78	9.828	0.76663	1.3044	2.53
64.869	1.29951	0.7719	9.73	0.000	0.70200	1.4245	0.00

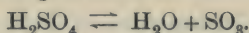
The contraction curve shows that the results are concordant, since any error in the density is magnified in calculating the contraction. Practically all the points lie on the curve; that at the 9.8 per cent. acid mixture is a little low, whilst those at the 28.5 and 29.6 per cent. acid mixtures are high and low respectively, due to bubble troubles.

Linebarger has pointed out that two non-associated liquids which mix without any chemical interaction should give no change of volume on mixing, or, at the most, only a slight expansion (*Amer. Chem. J.*, 1896, 18, 429). The specific volume-composition curve should thus be a straight line, or should lie just a little above the straight line. The specific gravity-composition curve for such "normal mixtures" would be part of a rectangular hyperbola. In the case of ether and sulphuric acid, we see from Fig. 1 that the specific volume curve lies considerably below the theoretical straight line joining the specific volumes of the two components. The observed specific volumes are up to 10 per cent. lower than the theoretical ones. The maximum deviation of the specific volume curve from the theoretical straight line occurs at no very definite point, but extends from about the 36 per cent. to the 60 per cent. acid mixture.

The contraction curve shows a fairly well defined maximum at about the 57 per cent. acid mixture, which corresponds with the composition of the complex $\text{H}_2\text{SO}_4 \cdot \text{Et}_2\text{O}$. Further, the contraction curve is approximately linear at both ends, as is to be expected, as with one component in large excess it is fair to assume that the whole of the minor constituent will be present in the solution as the complex, taking it for granted that one definite, dissociable complex is formed, and that the contraction is in some degree a measure of the amount of complex formed. When both constituents

are present in comparable amounts, part of the ether, say, will be present as free ether molecules, and part as ether molecules combined with the acid molecules to form the complex. If we extend the linear extremities of the contraction curve, we should presumably get the contraction curve that would be obtained if, throughout the whole range of mixtures, all the minor constituent were present solely as part of the complex. The maximum of this hypothetical curve—the point of intersection of the tangents to the real contraction curve at its two ends—is just about the 60 per cent. acid mixture. Hence the actual maximum of the contraction curve, and also the above hypothetical maximum, both point to the presence of the complex $\text{H}_2\text{SO}_4, \text{Et}_2\text{O}$ in the solutions.

In both the specific volume and the contraction curves there is a change in curvature just before we reach the pure acid end. This indicates that some further change occurs on the first additions of ether to the acid. This may be due to the fact that the acid was a little stronger than absolute sulphuric acid, or that it contains some impurities, or that absolute sulphuric acid is a highly associated liquid. Another probable reason for this irregularity lies in the evident checking of such dissociation as



The ethereal solutions, even those with a small percentage of ether, did not fume in the air. In this respect the addition of ether to the fuming acid is comparable to that of water. In any case, this equilibrium would disturb the simple relations expected for the other, namely, that between the acid and the ether molecules and the molecules of complex. All the properties examined of mixtures of ether and the "100 per cent. acid" show such peculiarities in the case of those solutions which contain 98 per cent. of acid or more.

The specific volume and the contraction curves for mixtures of ether and the "95 per cent. acid" are of the same general character as the above. Any abnormalities near the acid end, or near the ether end due to layer formation, were unnoticed through lack of data. The contraction on mixing at 30° is greater than that at 20° . This is perhaps the reverse of what would be expected if contraction is due to the formation of complexes, which is favoured by low temperatures. The association of the sulphuric acid, however, or the close proximity of the higher temperature to the boiling point of ether, may explain this fact. The maxima in the contraction curves at the two temperatures occur at the same mixture, which, as in the case of mixtures with the "100 per cent. acid," is that approximately corresponding with the complex $\text{H}_2\text{SO}_4, \text{Et}_2\text{O}$.

Electrical Conductivity.

Two series of experiments were carried out at 30°, one with mixtures of ether and the "100 per cent. acid," and the other using the "95 per cent. acid." Two conductivity cells of the ordinary type were used; one was a U-tube and had a cell constant of 26.31, whilst the other was a straight tube with a cell constant of 0.07023 (ohm, cm., units). It was not possible to always obtain a sharp minimum in the telephone, using one cell throughout the whole range of mixtures. The U-cell was used for all mixtures containing more than 50 per cent. of acid. The cells were standardised against solutions of potassium chloride, and the resistance box and slide wire were proved to be accurate within the limits of experimental error, which may be placed at 1 in 500 for the series as a whole.

TABLE II.

Specific Conductivity (κ) of Mixtures of Ether and "100 per cent. acid" at 30°; "x" denotes the percentage of acid in the ethereal mixtures.

x.	κ .	x.	κ .	x.	κ .	x.	κ .
0.000	0.000	43.564	0.001265	78.065	0.05438	96.004	0.05088
4.856	0.000000355	46.175	0.001800	84.844	0.07839	97.393	0.02707
6.630	0.000000850	52.111	0.004259	85.724	0.08023	97.592	0.024
10.054	0.000002302	58.312	0.01051	86.672	0.08308	98.002	0.01403
16.777	0.00001855	62.048	0.01643	91.388	0.08333	98.374	0.0123
21.779	0.0000545	64.869	0.02164	91.536	0.08275	98.683	0.01368
29.601	0.0002053	69.806	0.03178	92.955	0.07663	99.354	0.01891
39.125	0.0007196	72.016	0.03699	93.171	0.07506	100.000	0.02475

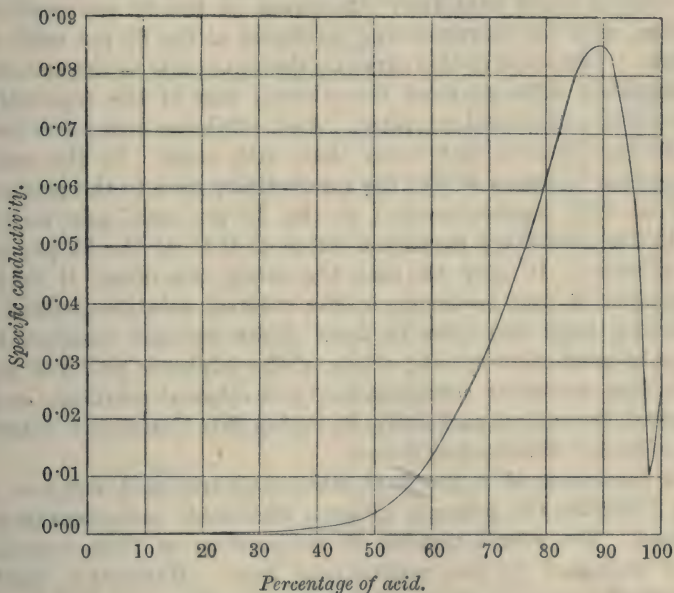
What at first seems a serious source of error in the mixtures with the "100 per cent. acid" is the fact that the conductivity of this acid is always changing (see above). The extreme variation in the conductivity of the acid used is about 4 per cent. This does not appear to be reflected in the conductivities of the mixtures made up from such acid. An attempt was made to reduce the readings to those that would be obtained by using an acid of constant conductivity, but the results were not satisfactory, judged by the regularity of the conductivity-composition curve. The results, as originally determined, are given in table II, the mean conductivity of the acid being taken as 0.02475.

The results obtained with the "100 per cent. acid" mixtures are plotted in Fig. 2. The points all lie on the curve. The conductivities of the mixtures of 97.6 and 98.4 per cent. acid decreased with the time, and hence are only approximate; yet the conductivity of the intermediate mixture with 98.0 per cent. acid was constant. The first noticeable point about the curve is the sharp descent to a

mixture of minimum conductivity of 0.01 approximately as ether is added to the acid. This is analogous to the case of sulphuric acid and water mixtures, the minimum conductivity of such being found at the 99.75 per cent. acid mixture by Kohlrausch, and at the 99.95 per cent. acid mixture by Knietsch. Further, this minimum conductivity of these sulphuric acid-water mixtures is also about 0.01 at 30°.

Hantzsch (*loc. cit.*) defines "absolute sulphuric acid" as the acid with the maximum freezing point; this acid is also that with the minimum conductivity. Its conductivity is raised by the addition

FIG. 2.



of water or ether. Had we used such acid, the minimum would have disappeared. It is, however, interesting to notice that the addition of ether (ethyl oxide) to acid of slightly more than 100 per cent. H_2SO_4 strength is equivalent to the addition of water (hydrogen oxide). Similarly, if we had used (Hantzsch's) absolute sulphuric acid, the abnormalities noticed in the case of the other physical properties for mixtures containing less than 2 per cent. of ether would probably have been eliminated (see also under density).

As more ether is added to the sulphuric acid, the rise to the maximum conductivity is very rapid, the maximum occurring about the mixture with 89 per cent. of acid, and having the value of 0.0855

approximately. From this point the conductivities of the mixtures fall rapidly until the value zero is reached, the conductivity of the pure ether. There is no approach to constant molecular conductivity for mixtures containing a small percentage of acid, the molecular conductivity-composition curve, like the specific conductivity-composition curve, becoming steeper the larger the amount of acid in the mixtures. Over the range from 50 to 90 per cent. acid mixtures, the conductivity is closely connected with the viscosity.

Comparing the above curve with the corresponding one for sulphuric acid-water mixtures, it is seen that in the latter case we have a rise to the maximum for the 30 per cent. acid mixture, including a small subsidiary maximum at the 92 per cent. acid mixture, with the corresponding minimum at the 85 per cent. acid mixture. The shape of this curve on the water side of the maximum is completely different from the ethereal side of the conductivity curve for the ether-acid mixtures. Also, sulphuric acid forms better conducting solutions with water than with ether. In the case of the aqueous solutions at 30°, the conductivity rises to the maximum value of 0.89 (approximately) at the 30 per cent. acid mixture, and to the subsidiary maximum value of 0.15 at the 92 per cent. acid mixture. It may be that the latter maximum is the one comparable to that occurring in the ethereal solutions, whilst the succeeding large maximum in more dilute aqueous solutions may be due to some other specific action of the sulphuric acid and water which does not occur correspondingly in ethereal solutions, and is expressed, but only superficially, by saying that water is an "electrolytic solvent," whilst ether is not.

The formation of a maximal ether-sulphuric acid mixture certainly indicates the presence of some dissociable complexes in such solutions. The actual number or composition of these complexes is not indicated by the conductivity data. Hantzsch's diethylhydronium sulphate may or may not be present.

The conductivities of the mixtures of ether with the "95 per cent. acid" furnish similar results to the above, but as they are incomplete, they are not tabulated. A complete study of the physical properties of ternary mixtures of ether, sulphuric acid, and water would be valuable.

Viscosity.

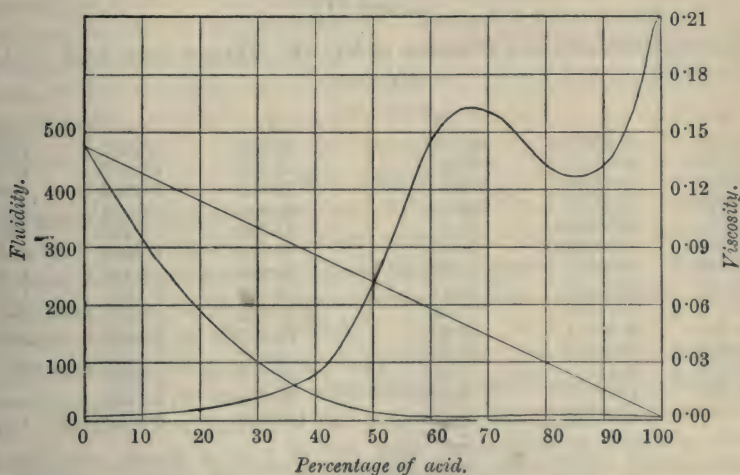
The specific viscosities of mixtures of "100 per cent. acid" and ether at 30° were found by the capillary tube method. A straight tube viscometer was used (compare Green, Trans., 1908, **93**, 2025). The time of flow was given by a stop-watch reading to a quarter

of a second, and could be relied on to one-tenth of a second. The working formula was:

$$\eta = A st - B \frac{s}{t},$$

where η is the specific viscosity (C.G.S. units), t the time of flow (seconds), s the density ($_{4}^{30^{\circ}}$) found from table I, and A and B are constants. The latter were found by calibrating the apparatus with water at temperatures of 20° , 25° , and 30° , and with ether at 30° , taking the specific viscosity of water as 0.010075, 0.008954, and 0.008029 respectively, and that of ether as 0.002134. The formula was checked for a very viscous liquid by determining the viscosity of a concentrated solution of sucrose, when the calculated value

FIG. 3.



agreed well with that obtained from Green's data (*loc. cit.*). At 30° the time of flow of water was 55.6 seconds, of ether 23.25, and of the sulphuric acid, 775 seconds. The viscosity of the "100 per cent. acid" remained constant throughout the series of experiments—contrast the density and conductivity. The second term in the formula—the kinetic energy correction—affects all the mixtures containing less than 55 per cent. of acid, but it is generally small compared with the first term, A being 0.0001481 and B 0.00993.

The results are given in table III and Fig. 3. The viscosity is denoted by η , the fluidity by f , and the percentage of acid in the mixture by x . In Fig. 3 the individual points are not shown, but they fit well on to the curves drawn. On adding the acid to the ether, the viscosity rises very slowly at first, but after the solution

contains more than 35 per cent. of acid it rises rapidly to a maximum value at the mixture with 67 per cent. of acid. As the acid concentration is further increased, the viscosity falls to a minimum at the 85 per cent. acid mixture, and afterwards rises regularly to about the 98.5 per cent. acid mixture, and thence less steeply to the highest viscosity observed—that of the pure acid. This last deviation of the curve is comparable to those noticed in the density and conductivity curves near the acid end; in all these cases the underlying cause is certainly the same (see above).

The fluidity-composition curve, also drawn in Fig. 3, shows the effect of the addition of the first acid to the ether. According to Bingham (*Amer. Chem. J.*, 1906, **35**, 195), the viscosity-composition curve of a simple mixture without complex formation would be a

TABLE III.

Specific Viscosity and Fluidity at 30° of "100 per cent. acid"-ether Mixtures.

<i>x.</i>	<i>η.</i>	<i>f.</i>	<i>x.</i>	<i>η.</i>	<i>f.</i>
0.000	0.002134	468.6	69.806	0.1606	6.227
6.630	0.00273	366.3	72.016	0.1567	6.381
9.828	0.003096	322.9	78.065	0.1388	7.202
16.777	0.00436	229.4	84.844	0.1272	7.861
21.779	0.005790	172.7	85.724	0.1272	7.861
29.601	0.009824	101.8	91.536	0.1382	7.236
39.125	0.02194	45.58	92.955	0.1452	6.887
43.564	0.03480	28.74	96.004	0.1692	5.909
46.175	0.04752	21.04	97.393	0.1872	5.343
49.326	0.06701	14.92	97.592	0.1897	5.271
52.111	0.08788	11.38	98.002	0.1963	5.093
58.312	0.1345	7.435	98.683	0.2030	4.926
62.048	0.1537	6.506	99.354	0.2069	4.832
64.869	0.1615	6.193	100.000	0.2100	4.762

rectangular hyperbola, and the corresponding fluidity curve a straight line. The case is analogous to that of the density and specific volume curves. The marked deviation of the fluidity curve for the ether-acid mixtures from the straight line is greatest between the 35 per cent. and the 45 per cent. acid mixture.

In most cases, maxima in the viscosity-composition curves of mixtures have been assumed to correspond with association of the molecules of the mixture to form complex molecules, and such maxima occur frequently at mixtures of definite molecular composition, and their position is fairly constant within a more or less considerable temperature range (compare Dunstan, *Trans.*, 1904 to 1909). Hence there would seem to be no doubt that the maximum in the ether-acid viscosity curve does indicate the presence of some complex formation in the solution. The maximum occurs at the mixture of 67 per cent. acid, approximately corresponding

with the complex $3\text{H}_2\text{SO}_4, 2\text{Et}_2\text{O}$. However, if Bingham's view is correct, the deviation of the viscosity curve from the theoretical hyperbola is more important than the actual maximum. This deviation is greater in the case of mixtures with a little less than 67 per cent. of acid, as is seen by imagining the two ends of the above viscosity curve to be continued until they meet. Also, the amount of electrolytic dissociation suffered by the complex would affect the position of the maximum. Hence, whether the above complex is formed in the solutions is very doubtful.

The position of the mixture of highest conductivity is about that of the minimum in the viscosity curve, for even if there are fewer ions from the smaller amount of complex in this mixture, there is the lower viscosity. In order to obtain some idea as to the interdependence of the conductivity (κ) and the viscosity (η), the product of these two magnitudes ($\eta\kappa$) was plotted against the percentage of acid in the mixture (x). From the 59 per cent. to the 89 per cent. acid mixture the graph is a straight line, the protuberance of the viscosity curve in the same range being completely eliminated. Over this range, therefore,

$$\begin{aligned}\eta\kappa &= \alpha x + \beta, \\ \text{or } \kappa &= \alpha x f + \beta f,\end{aligned}$$

where α and β are constants, and f denotes the fluidity. Assuming that the conductivity is directly proportional to the ionic concentration and inversely proportional to the viscosity, we see that over this range the ionic concentration is directly proportional to the amount of acid in the mixture.

The viscosity composition curve for these ether-acid mixtures is exactly similar to that for water-sulphuric acid mixtures (Dunstan and Wilson, *Trans.*, 1907, **91**, 83). For the latter mixtures the maximum occurs at the 85 per cent. acid mixture, corresponding with $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, and the minimum at the 95 per cent. acid mixture, approximating to $3\text{H}_2\text{SO}_4, \text{H}_2\text{O}$. The position of the minimum probably has little significance, but the hydrate, $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, has been indicated by every physical property of the mixtures examined.

Surface Tension.

For the measurement of the surface tension of the mixtures of ether and the "100 per cent. acid," the method of drops was used. The changes in the surface concentration at the top of a mixture in a very small capillary tube seemed so uncertain and might be so large that the ordinary measurement of the rise of liquid in such a tube was not attempted. The mixture was allowed to drop from the end of a thick capillary tube of 6.822 mm. external diameter, the end of which was ground flat. The drops (6 to 12)

were collected in a weighing bottle. The whole was placed in a wider glass tube containing some of the same mixture, so that the drops fell in an atmosphere saturated with the vapour of the mixture. Loss of weight of the drops by evaporation was thus reduced to a minimum. The whole apparatus was placed in a thermostat with glass sides, and kept at 30°.

TABLE IV.

*Surface Tensions (dynes per cm.) of Mixtures of Ether and
"100 per cent. acid" at 30°.*

Percentage of acid.	Surface tension.	Percentage of acid.	Surface tension.
100·000	50·70	61·186	38·63
98·683	49·03	50·140	33·39
96·004	48·94	44·631	30·70
93·171	48·53	43·123	29·84
89·550	48·64	32·249	24·39
77·810	46·88	21·361	19·51
70·913	43·72	10·942	16·0
61·810	38·96	0·000	15·61

Preliminary experiments with water and benzene showed that the weight of a drop decreases as the time of its formation is increased—the true drop is the infinitely slow drop. For each liquid, however, after the time of formation of its drop has reached a certain limiting value, the weight of the drop is practically constant. Further experiments with the above liquids and with ether, aniline, carbon disulphide, and nitrobenzene—all liquids of known surface tension—showed that the weight of the drop was directly proportional to the surface tension. After a comparison of the values obtained by different observers using standard methods, the surface tension of water at 30° was taken as 71·81 dynes per cm. Plotting the surface tensions of the above liquids against the weights of their drops, it was seen that the straight line through the zero point (0, 0) and through the water point (71·81, 0·09315) passed practically through all the points, at any rate, well within the limits of experimental error. The basis of the work is thus the surface tension of water at 30°, and the above value for it is probably correct to within $\pm 0\cdot5$ per cent. Thus, if m is the weight of the drop of a mixture, then its surface tension, α , is given by

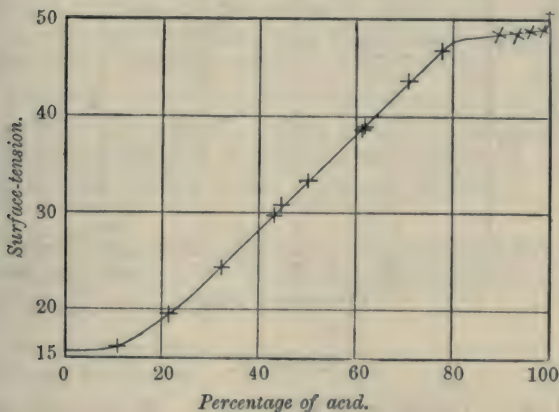
$$\frac{\alpha}{m} = \frac{71\cdot81}{0\cdot09315}.$$

The error in duplicate determinations for the weight of a drop was, on the average, $\pm 0\cdot2$ per cent., although it was greater than this for mixtures very rich in ether, for example, up to ± 2 per cent. On the whole, this is well within the limits of accuracy

obtained for measurements of surface tension of liquids other than water by different observers. The method of drops would therefore seem to be particularly applicable for the measurement of the surface tension of liquid mixtures.

The results for the surface tensions of ether-"100 per cent acid" mixtures are given in table IV and Fig. 4. Over a large range, from the 20 per cent. to the 80 per cent. acid mixture, the surface tension varies linearly with the composition. The same is true in the range from the 84 per cent. to the 98 per cent. acid mixture, where the surface tension is also very nearly constant. Above the 98.5 per cent. acid mixture, the surface tension rises to that of the pure acid, the curve thus presenting the common irregularity near the acid end. The surface-tension curve gives little indication of

FIG. 4.



complex formation in the mixtures, the regularity of the middle section being exceptional as compared with the other physical properties examined.

Vapour Pressure.

The vapour pressures of mixtures of the "95 per cent. acid" and ether were observed at three temperatures, approximating to 20°, 25°, and 30° respectively. From the vapour pressure-temperature graphs the values of the vapour pressures at these three temperatures were read off. The mixtures were placed over mercury in a U-tube barometer, with a water-jacket kept at the desired temperature. The vapour pressures were accurate to the nearest millimetre of mercury. However, by expressing the vapour pressures of the mixtures at any one temperature as fractions of the vapour pressure of ether at this same temperature, it was seen that for

a given mixture this relative vapour pressure was independent of the temperature, at least, within the temperature range considered. The vapour pressures of ether at 20°, 25°, and 30° were taken as 442, 544, and 647 mm. respectively; from these the relative vapour pressures of the various mixtures were calculated, and are given in table V and Fig. 5.

FIG. 5.

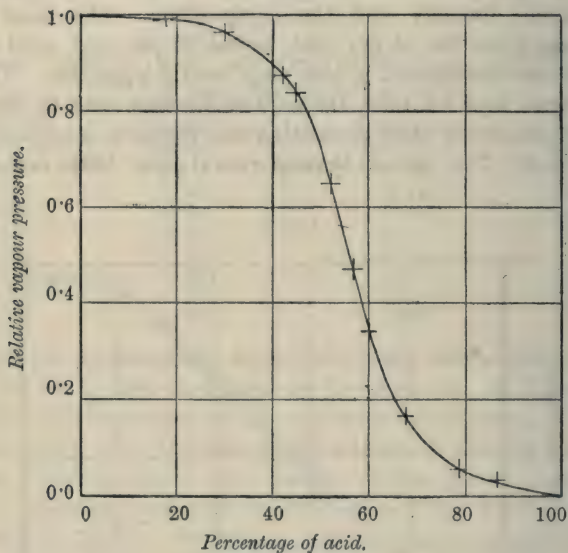


TABLE V.

Relative Vapour Pressures of Mixtures of "95 per cent. acid" and Ether between 20° and 30°.

Grams of acid in 100 grams of mixture.	Relative vapour pressure.	Grams of acid in 100 grams of mixture.	Relative vapour pressure.
100.00	0.000	43.26	0.529
82.01	0.006	40.11	0.658
70.11	0.034	32.31	0.835
57.94	0.124	21.19	0.944
55.39	0.161	13.24	0.967
48.00	0.351	0.00	1.000

As the acid is added to the ether, the vapour pressure continuously decreases from that of pure ether to zero, the "95 per cent. acid" having practically no vapour pressure at the temperatures used. This fall of vapour pressure is most rapid between the 40 per cent. and 50 per cent. acid mixtures, where the curve is straight. The curve is also linear at both ends, as expected according to Raoult's law. The general shape of the whole curve supports the

idea that a complex is formed, and in increasing amounts as we approach the equimolecular mixture, at about which point also is the curve most removed from the straight line joining the two ends of the curve, that is, from the theoretical vapour pressure curve. Hence some complex, possibly $\text{Et}_2\text{O}, \text{H}_2\text{SO}_4$, exists in the mixtures. The vapour pressure curve for mixtures of sulphuric acid and water is perfectly analogous to the above curve.

Specific Heats of Mixtures of Ether and "100 per cent. acid."

Such a series was attempted, but with the apparatus tried satisfactory results were not obtained; sufficient data were found to prove that the specific heats of the mixtures fell below those calculated from the normal mixture rule, the maximum deviation occurring for mixtures with between 60 and 70 per cent. of acid.

In the case of none of the physical properties examined do solutions of ether and sulphuric acid follow the "normal mixture" laws. The actual number and composition of such complexes as are most probably formed in the solutions cannot be given with certainty. From the marked analogy in several instances to water-sulphuric acid solutions, it is possible, however, that at least the complex $\text{H}_2\text{SO}_4, \text{Et}_2\text{O}$ exists in the ether-acid mixtures.

In conclusion, the author desires to express his indebtedness to Professor Masson and to Dr. Steele for their ever-ready help and kindly interest in the work.

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LXXVIII.—*Isomeric Monothiophosphates.*

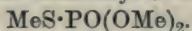
By WILLIAM GIDLEY EMMETT and HUMPHREY OWEN JONES.

IN making attempts to prepare an isomeride of trisodium monothiophosphate, $\text{PS}(\text{ONa})_3$, having the formula $\text{NaS} \cdot \text{PO}(\text{ONa})_2$, the methyl esters of the corresponding acids were examined with a view to subsequent saponification.

These esters were prepared, in the first place, by Pistschimuka (*Ber.*, 1908, **41**, 3854); the method of preparation has been improved, their properties have been examined more minutely, and additional evidence as to their constitution has been obtained.

For convenience of description, the prefix α is given to that

compound in which the sulphur is doubly linked to phosphorus, and β to the compound in which sulphur is linked to phosphorus and to an electropositive element or radicle; thus trimethyl α -thiophosphate, $\text{PS}(\text{OMe})_3$, and trimethyl β -thiophosphate,



Pistschimuka prepared the α -ester by the action of sodium methoxide on thiophosphoryl chloride. This ester gave a silver salt, $\text{AgO}\cdot\text{PS}(\text{OMe})_2$, by the action of silver nitrate, which, on treatment with methyl iodide, yielded trimethyl β -thiophosphate. The authors found that when preparing the α -ester by the above method, a certain amount of β -ester is also formed, the latter being detected readily by its property of forming yellow silver mercaptide on warming with silver nitrate solution. A study of the origin of the β -ester showed that the pure α -ester readily undergoes isomeric change when heated to about 100° .

The most interesting properties of these esters are the reaction with methyl iodide at 100° , giving trimethylsulphonium iodide, and their behaviour towards mercuric chloride, the α giving an additive compound, and the β a double compound of mercury mercaptide and mercuric chloride. Experiments on saponification, under varying conditions, demonstrated the great difficulty of removing the last methyl group from the molecule. From the α -ester, mono- and di-sodium salts were easily obtained; but the trisodium salt prepared by Wurtz (*Ann. Chim.*, **30**, 472) was only once isolated in small quantity from the products of saponification.

The β -ester gave a monosodium salt, isomeric with that obtained from the α , and since this reacted with silver nitrate to form silver mercaptide, it probably has the formula $\text{MeS}\cdot\text{PO}(\text{OMe})\cdot\text{ONa}$.

EXPERIMENTAL.

Preparation of Trimethyl α -Monothiophosphate.

For this purpose, the action of sodium methoxide on thiophosphoryl chloride was used, according to Pistschimuka's method. The theoretical quantity of sodium is dissolved in a minimal amount of methyl alcohol, and the cooled solution is added drop by drop to the thiochloride. Precipitated sodium chloride is filtered off, and the liquid immediately distilled on the water-bath in order to reduce isomeric change to a minimum. Fractionation under diminished pressure gives a 66 per cent. yield of the ester, boiling at $75^\circ/3$ mm. or $80^\circ/12$ mm. (Pistschimuka gives $82^\circ/20$ mm.). No phosphorescence was observed in the vapours from the fuming liquid. Specific gravity determinations gave values of 1.2112 at

10.5°, and 1.2053 at 15° (Pistschimuka gives 1.2192 at 0°). Its solubility in cold water is very slight, increasing somewhat on heating, and giving a solution neutral to litmus. The ester is miscible with alcohol or ether in all proportions.

A dilute aqueous solution is stable towards hot solutions of salts of copper, lead, barium, nickel, cobalt, and manganese, and ammonium molybdate in nitric acid solution has no action, even on boiling.

Ferric chloride gives an orange colour on heating, and mercurous nitrate a black precipitate in the cold; the latter salt reacts similarly towards all the sulphur-phosphorus compounds examined. With mercuric chloride, a white, insoluble, additive compound is produced, having the formula $\text{PS(OMe)}_3 \cdot 2\text{HgCl}_2$ (Pistschimuka, *loc. cit.*), which we have confirmed. This compound is soluble in hot acetone, and is easily crystallised from this solvent, giving clusters of needles, which melt and effervesce at 107–108°.

The oxidising action of hot fuming nitric acid liberates the sulphur as sulphuric acid; the phosphorus, however, is not converted into phosphoric acid.

The silver salt, $\text{AgO} \cdot \text{PS(OMe)}_2$, mentioned by Pistschimuka, was readily prepared by adding the ester to a hot aqueous solution of silver nitrate, the yield being 75 per cent. of the theoretical; a small quantity of silver sulphide is precipitated. An analysis of the salt showed that it was represented by the formula $\text{C}_2\text{H}_6\text{O}_3\text{SPAg}$. The salt separates from hot water in very fine, long, white, silky needles, melting and decomposing at 144°.

Preparation of Trimethyl β -Monothiophosphate.

The calculated quantity of methyl iodide, mixed with an equal volume of ether, is added to silver dimethyl α -thiophosphate, and the mixture heated to 100° in a sealed tube for two hours. Fractionation of an ethereal extract of the mass gave an 83 per cent. yield of a colourless liquid, boiling at 99–100°/3 mm. (Pistschimuka gave 103°/12 mm.). By this method, very little action between methyl iodide and the β -ester occurs.

An attempt at preparation of the ester from sodium dimethyl α -thiophosphate and methyl iodide failed, owing to formation of trimethylsulphonium iodide.

Estimation of carbon, hydrogen, and phosphorus showed that the ester has the composition PSO_3Me_3 .

The differences between the isomeric esters, as shown by the following data, are very marked.

Molecular Refractions.

	Density, (<i>d.</i>)	$n_{\text{H}_2\text{O}}$	$\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$	n_{Na}	$\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$
α -Trimethyl ester.....	1.2112 at 10.5°	1.45522 at 10.5°	46.2	1.45830 at 10.5°	46.4
β -Trimethyl ester.....	1.2565 at 10°	1.46598 at 10°	45.3	1.46864 at 10°	45.5

The β -ester does not fume in moist air; its odour recalls that of parsnips, and it is readily soluble in cold water.

With aqueous or alcoholic silver nitrate in the cold, it very slowly gives a white precipitate, the reaction not being complete after several hours. This precipitate was shown to consist of a compound of silver methylmercaptide with silver nitrate, in the approximate proportions of 2:1 (figures from an analysis, 10:5.5). On heating a suspension of this compound in water, or on adding the β -ester to a boiling aqueous solution of silver nitrate, yellow silver mercaptide is formed immediately. This reaction, although useful as a qualitative means of recognising the β - in presence of the α -ester, cannot be applied quantitatively on account of its incompleteness. The metallic salts with which the β -ester in aqueous solution reacts are:

Silver nitrate: as above.

Ferric chloride: orange coloration gradually on boiling.

Mercurous nitrate: black precipitate in the cold.

Mercuric chloride gives a faint white turbidity in the cold, and a white precipitate on heating, which, on analysis, gave the following results:

Found: Hg=70.1; Cl=17.3; C=3.04; H=0.77.

$\text{Hg}(\text{CH}_3\text{S})_2, 2\text{HgCl}_2$ requires Hg=71.8; Cl=17.0; C=2.87;
H=0.72 per cent.

Isomeric Change of Trimethyl α -Thiophosphate into the β -Ester.

In the study of this change, the presence of β -ester was detected by its reaction with silver nitrate.

On heating the pure α -ester to 100° in a sealed tube alone, or with either methyl alcohol, a solution of sodium methoxide, distilled water, or hydrochloric acid in methyl alcohol, a considerable quantity of the β -modification (approximately 50 per cent.) was produced. Appreciable amounts were obtained after heating for half-an-hour, but the quantity apparently reached a maximum after three to four hours. In no case was complete conversion to the β -ester observed. As a rough indication of the extent of change, the proportion soluble in cold water was noted.

An attempt to study the change quantitatively by estimating the amount of silver mercaptide given with silver nitrate, failed on account of the small rate of formation of the precipitate. Also, the possibility of determining the state of equilibrium by the influence of the isomeric esters on the rotatory power of ethyl tartrate was not realised.

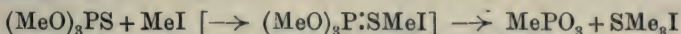
Action of Methyl Iodide on the Esters.

On heating the α -ester with methyl iodide in a sealed tube to 100° , crystals began to form after one and a-half hours, and after five hours' heating a large quantity of crystals was obtained, embedded in a gummy mass.

Several recrystallisations from alcohol did not free the product entirely from phosphorus; as finally obtained, it melted and sublimed at $209\text{--}210^\circ$, and analysis showed it to be trimethylsulphonium iodide, contaminated with a small amount of impurity.

The alcoholic mother liquors gave a gummy substance, insoluble in ether, and only sparingly soluble in alcohol; it was, however, readily soluble in water, giving a strongly acid solution. This solution gave the ammonium molybdate reaction for phosphoric acid, and with magnesia mixture produced a white, crystalline precipitate, the quantity of which was largely increased on boiling.

The substance was shown to contain no sulphur, and may be regarded as being derived from methyl metaphosphate, formed as below:

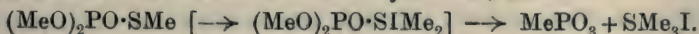


by the addition of water or methyl alcohol.

Distillation of the gum under 10 mm. pressure, or even in a carbon-liquid air vacuum, caused decomposition, a sticky residue, strongly acid to litmus, being obtained, which gives a marked molybdate reaction, and a white, gelatinous precipitate with silver nitrate; these reactions show that it was probably metaphosphoric acid.

When the β -ester was treated with methyl iodide under the same conditions as the α -ester, white crystals began to form after ten minutes, and the reaction appeared complete in one to two hours.

A gum having the same properties as that obtained in the corresponding reaction of the α -ester was formed, along with the crystals. An iodine estimation in the latter gave $\text{I} = 62.6$ per cent; its properties showed that it was trimethylsulphonium iodide ($\text{I} = 62.2$ per cent.), and the reaction is regarded as being of the same nature as that between the α -ester and methyl iodide, thus:



The greater velocity of the reaction is understood from the constitution of the β -ester; or it may be due to the α -ester undergoing isomeric conversion to the β -ester before reacting with methyl iodide.

Action of Sodium Methoxide on the Esters. Sodium Dimethyl α -Monothiophosphate.

By the action of sodium methoxide on the α -trimethyl ester in the cold, the compound $\text{NaO} \cdot \text{PS}(\text{OMe})_2$ (Pistschimuka) is formed. It is also readily obtained by the action of four molecules of sodium methoxide on one of thiophosphoryl chloride. It forms fine, silky needles, which do not melt without decomposition when freshly prepared; but after exposure to air for a few days, water is absorbed, and the substance then melts partly at 35.5° . It is very soluble in alcohol, methyl alcohol, or water, and on this account is not easily obtained pure. The aqueous solution is neutral to litmus.

By the action of heat, sodium metaphosphate is produced as a glassy mass, and white fumes, having the odour of the β -trimethyl ester, were evolved.

The following reactions with dilute aqueous solutions of inorganic reagents were obtained:

Copper sulphate: pale green precipitate, unchanged on boiling.

Ferric chloride: orange coloration, slightly deeper on boiling.

Nickel sulphate: pale bluish-grey precipitate, unchanged on boiling.

Cobalt nitrate: no precipitate in the cold, pinkish precipitate on heating.

Silver nitrate: faint white precipitate, turning light brown on heating.

Iodine solution: decolorised.

Mercuric chloride: faint white turbidity.

Mercurous nitrate: greyish-black precipitate.

Lead and manganese salts have no action.

When sodium dimethyl α -thiophosphate is heated with methyl iodide at 100° , and the mass subjected to distillation, trimethylsulphonium iodide is readily obtained in a state of purity.

Sodium Dimethyl β -Thiophosphate.

On mixing sodium methoxide in methyl-alcoholic solution with the pure β -ester in molecular proportions, a rapid evolution of gas (methyl ether) takes place, and the liquid sets to a solid. After washing the mass with ether and crystallising the residue from ethyl alcohol, white, flaky crystals were obtained. These were moderately soluble in ethyl alcohol, although less so than the corresponding

compound from the α -ester; they were also very soluble in methyl alcohol, but insoluble in ether. The compound, as such, has no melting point.

The addition of silver nitrate to a solution gives a white precipitate slowly in the cold, changing, on heating, to bright yellow silver mercaptide. The white precipitate is probably identical with that obtained by the action of silver nitrate on the β -ester in the cold. These reactions indicate the formula $\text{NaO} \cdot \text{PO}(\text{SMe}) \cdot \text{OMe}$ for the salt. Solutions of copper sulphate and of lead acetate have no action.

Saponification of the Esters.

A number of experiments were performed with a view to the preparation of two isomeric sodium salts, as mentioned above. The conditions of the experiments were varied, first, as regards the nature of alkali, sodium hydroxide and sodium hydrogen sulphide being used in turn; secondly, as regards proportion and concentration of alkali, namely, the proportion from 3 to 6 molecules to one of ester, and the concentration from $N/2$ to $2N$; then, as regards pressure and temperature, the experiments being conducted either at atmospheric pressure or in sealed tubes, the temperature varying from 100° to 150° ; and finally as regards solvent, alcohol and water being employed.

In the majority of experiments, inconclusive results were obtained, as the products isolated could not be purified, probably on account of formation of isomorphous mixtures. In fact, the only new compound prepared of which a satisfactory analysis could be made, was the sodium dimethyl salt from the α -ester.

Disodium Methyl α -Thiophosphate.

The α -ester is mixed with six equivalents of alcoholic sodium hydrogen sulphide, heated in a closed bottle for eight hours at 100° , and then evaporated in a vacuum over calcium chloride. After a day, fine, long prisms separated, which were washed with cold ethyl alcohol, and recrystallised from methyl alcohol:

Found: C = 3.92; H = 5.32; S = 11.94; P = 11.13.

$\text{Na}_2(\text{CH}_3)\text{PSO}_3 \cdot 6\text{H}_2\text{O}$ requires C = 4.28; H = 5.36; S = 11.43;
P = 11.07 per cent.

On heating, the crystals melted at 49° , and a vapour having the odour of the β -ester was evolved, leaving an opaque solid residue, which gave the reactions of sodium pyrophosphate.

A quantitative experiment on the product of ignition gave the following figures:

0.5340 gave 0.2515 $\text{Na}_4\text{P}_2\text{O}_7$. Na = 16.0.

$\text{Na}_2(\text{CH}_3)\text{PSO}_3 \cdot 6\text{H}_2\text{O}$ requires Na = 16.4 per cent.

The salt is very sparingly soluble in cold ethyl alcohol, and melts under the hot solvent; it is more soluble in methyl alcohol, and very soluble in water.

An aqueous solution is alkaline to litmus, and gives the following reactions:

Copper sulphate: yellowish-green solution; brownish-black precipitate on boiling.

Silver nitrate: with a trace, yellow-orange precipitate; soluble in excess of thiophosphate, giving a deep reddish-brown solution, unchanged on heating. Excess of silver nitrate gives an orange precipitate, rapidly changing to brown and black in the cold.

Cobalt nitrate: pink solution, unchanged on boiling.

Ferric chloride: orange coloration, becoming paler on boiling.

Mercuric chloride: with a trace, gives a yellow solution; excess gives an orange-white precipitate.

Lead acetate: heavy, white precipitate; easily soluble in excess of thiophosphate; the precipitate is unchanged on boiling.

Further attempts to replace the last methyl group by sodium met with complete failure.

A few notes on the methods of analysis adopted may be of some use. For the determination of sulphur in those compounds containing no carbon, oxidation by hydrogen peroxide in an ammoniacal solution (Kubiersky, *J. pr. Chem.*, 1885, [ii], **31**, 93) gave good results.

Kubiersky's method of determining water of crystallisation in these salts by heating with copper oxide only gave very approximate values; the determination is best carried out by heating in a combustion tube containing lead chromate, and collecting the water in a calcium chloride tube.

An attempt to estimate methoxyl in the esters, and in the sodium methyl salts, by Zeisel's method, taking due precautions for removal of hydrogen sulphide, was without success, presumably on account of formation of methyl mercaptide.

The estimation of sulphur in those compounds having an alkyl group attached to the sulphur atom by Carius's method requires a very high temperature, since sulphones are probably formed.

The expenses of the work have been largely defrayed by grants from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

UNIVERSITY CHEMICAL LABORATORY,
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LXXIX.—6-Nitro-3:4:3':4'-tetramethyldiphenyl.

By ARTHUR WILLIAM CROSSLEY and CHARLES HERBERT
HAMPSHIRE.

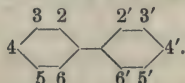
WHEN *o*-xylene is added to fuming nitric acid, mono- and di-nitro-*o*-xylenes are produced (Trans., 1909, **95**, 202) according to the conditions of experiment. If, on the other hand, fuming nitric acid is added to *o*-xylene (*ibid*, p. 217; Proc., 1909, **25**, 162), considerable quantities of the latter are recovered unchanged, whilst some is transformed into mono- and di-nitro-*o*-xylenes, and a small amount into a substance, $C_{16}H_{17}O_2N$, melting at 115° , which has now been proved to be nitro-3:4:3':4'-tetramethyldiphenyl.* The formation of this substance would appear to be due to an oxidising action of the nitric acid, whereby one hydrogen atom is removed from each of two *o*-xylene rings, which then couple together.

The proof that the two xylene nuclei are directly united through carbon atoms of the rings, and not by those of the methyl groups, has been established, in the first place, by oxidation with dilute nitric acid, when the substance $C_{16}H_{17}O_2N$ yields a nitrotetracarboxylic acid as a well-defined, crystalline compound. This fact definitely establishes the presence of four methyl groups in the original substance, which is, therefore, a nitrotetramethyldiphenyl.

The positions of the methyl groups have been ascertained in the following manner. When the nitrotetramethyldiphenyl is reduced with tin and hydrochloric acid, it gives an *aminotetramethyldiphenyl*, from which, by diazotisation and treatment with stannous chloride, the nitrogen can be eliminated and a tetramethyldiphenyl produced. This hydrocarbon has also been synthesised from *o*-xylene as a starting point, by first preparing 4-nitro-*o*-xylene, which was reduced to 4-amino-*o*-xylene, and the latter diazotised and treated with potassium iodide. The resulting 4-iodo-*o*-xylene was then heated with copper powder according to the directions of Ullmann (*Annalen*, 1904, **332**, 38), when 3:4:3':4'-tetramethyldiphenyl was obtained, identical with the substance prepared by



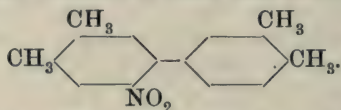
* The rings are numbered in accordance with the following scheme :



eliminating the nitro-group from the nitrotetramethyldiphenyl, formed during the interaction of *o*-xylene and fuming nitric acid.

Attempts were made to obtain 6-nitro-3:4:3':4'-tetramethyldiphenyl (m. p. 115°) by the direct nitration of the synthetic tetramethyldiphenyl, but under the conditions used there resulted only the tetranitrotetramethyldiphenyl described on page 724 as being formed by the further nitration of nitrotetramethyldiphenyl.

The exact position of the nitro-group in nitro-3:4:3':4'-tetramethyldiphenyl has not, so far, been ascertained, but there is considerable indirect evidence to show that it occupies position 6:



Schultz (*Annalen*, 1881, **207**, 352) has shown that by direct substitution a nitro-group entering the diphenyl molecule takes up a position ortho or para, but not meta, with respect to the ring union. In the present case the para-position is occupied by a methyl group, and consequently the nitro-group, if it cannot enter the meta-position 5, must be attached to either of the carbon atoms 2 or 6, that is, ortho to the ring union.

Further, the nitrodiphenyltetracarboxylic acid produced by oxidation of nitrotetramethyldiphenyl is capable of being directly esterified to give a tetraethyl ester. The hindering effect on esterification of a nitro-group in the ortho-position with respect to a carboxyl group is well known, and hence it would appear that position 6 is the one which must be occupied by the nitro-group in nitrotetramethyldiphenyl.

EXPERIMENTAL.

Twenty-five grams of fuming nitric acid* were added drop by drop to 10 grams of *o*-xylene contained in a flask immersed in a freezing mixture. The operation required about forty minutes, during which time the temperature was maintained at -10°. The dark brown reaction product was poured into water, when a pale yellow oil separated on the top of the liquid, which was removed, and the residue extracted three times with ether. The extract was mixed with the above-mentioned oil, washed with dilute sodium hydroxide solution, then with water, dried over calcium chloride, and the ether evaporated. The pale brown oil obtained in this

* The nature of the fuming nitric acid employed has a great influence on the amount and character of the products produced. The acid used in the experiments described in this communication had $D_{13.5}^{20}$ 1.505, and on titration with sodium hydroxide solution showed an acid value corresponding with 91.5 per cent. HNO_3 .

manner from 50 grams of *o*-xylene was submitted to prolonged distillation in steam, when an almost colourless, light oil passed over readily, and a heavy, yellow oil (A) slowly collected at the bottom of the receiver. On cooling, the latter set to a gummy mass, which was triturated with small quantities of ether, when it yielded 4.2 grams of a pale yellow powder. This was crystallised from alcohol, and analysed:

0.1219 gave 0.3383 CO₂ and 0.0764 H₂O. C=75.68; H=6.96.

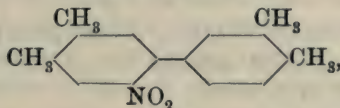
0.2775 „ 13 c.c. N₂ (moist) at 15° and 751 mm. N=5.42.

C₁₆H₁₇O₂N requires C=75.29; H=6.66; N=5.49 per cent.

The molecular weight was determined by the cryoscopic method, using benzene as solvent.

Found: M.W.=251, 253. C₁₆H₁₇O₂N requires M.W.=255.

6-Nitro-3:4:3':4'-tetramethyldiphenyl,



dissolves readily in the cold in chloroform, acetone, ethyl acetate, or benzene, and fairly readily in light petroleum (b. p. 80—100°) or alcohol on warming, separating from either of the latter solvents in clusters of stout, yellow, flattened needles, melting at 115°.

The steam distillate from which the solid A had been removed (see above) was extracted with ether, and the residual oil distilled in air, when 28 grams of unchanged *o*-xylene and 10 grams of a liquid of higher boiling point were obtained. The latter oil was accumulated from a large number of experiments, when 263 grams were submitted to the process of separation previously described (Trans., 1909, 95, 215), and yielded 52 grams of pure 4-nitro-*o*-xylene, 30 grams of pure 3-nitro-*o*-xylene, and varying quantities of the isomeric dinitro-*o*-xylenes.

Oxidation of Nitrotetramethyldiphenyl.

Two grams of nitrotetramethyldiphenyl were heated in a sealed tube with 20 c.c. of dilute nitric acid (D 1.15) for four hours at 170—180°. A clear green liquid resulted, which on shaking set to a mass of small, white crystals. After washing with water and spreading on porous plate, 2.9 grams were obtained, whereas the theoretical amount, if a tetracarboxylic acid is formed, should be 2.94 grams. This solid was purified by several crystallisations from water, and analysed, after being dried in air:

0.1340 gave 0.2391 CO_2 and 0.0424 H_2O . $\text{C}=48.66$; $\text{H}=3.51$.

0.2367 „ 6.8 c.c. N_2 (moist) at 8° and 752 mm. $\text{N}=3.44$.

$\text{C}_{16}\text{H}_9\text{O}_{10}\text{N}, \text{H}_2\text{O}$ requires $\text{C}=48.85$; $\text{H}=2.8$; $\text{N}=3.56$ per cent.

6-Nitrodiphenyl-3:4:3':4'-tetracarboxylic acid is readily soluble in the cold in alcohol or acetone, almost insoluble in benzene or chloroform, and crystallises from water in small clusters of white, hair-like needles. The melting point is somewhat indefinite, as it is also a decomposition point, but when determined in the ordinary manner, heating first as rapidly as possible to 200° and then slowly, softening commences at 220° , gas is evolved at 225° , and a clear liquid is formed at 228° .

The water of crystallisation in the acid was determined by heating to 100° in an air-bath:

1.1388 lost 0.0527 H_2O . $\text{H}_2\text{O}=4.63$.

$\text{C}_{16}\text{H}_9\text{O}_{10}\text{N}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O}=4.60$ per cent.

The molecular weight of the acid was found by titration with $\text{N}/10$ -potassium hydroxide solution to be 390, whereas the calculated for $\text{C}_{16}\text{H}_9\text{O}_{10}\text{N}, \text{H}_2\text{O}$ is 393.

The *silver* salt was prepared by adding silver nitrate to a solution of the potassium salt. It is a faintly yellow, curdy precipitate, which decomposes rather vigorously when heated, and with considerable increase in bulk:

0.1198 gave 0.0640 Ag. $\text{Ag}=53.42$.

$\text{C}_{17}\text{H}_5\text{O}_{10}\text{NAg}_4$ requires $\text{Ag}=53.80$ per cent.

The *tetraethyl* ester, obtained by heating the silver salt with ethyl iodide in dry benzene solution or by direct esterification of the acid, is readily soluble in the cold in benzene, chloroform, acetone, or ethyl acetate, and crystallises from alcohol in clusters of colourless, transparent, irregular needles, melting at $126\text{--}127^\circ$:

0.1268 gave 0.2739 CO_2 and 0.0628 H_2O . $\text{C}=58.91$; $\text{H}=5.50$.

$\text{C}_{24}\text{H}_{25}\text{O}_{10}\text{N}$ requires $\text{C}=59.14$; $\text{H}=5.13$ per cent.

Nitration of Nitrotetramethyldiphenyl.

Finely powdered nitrotetramethyldiphenyl was gradually added to fuming nitric acid, when it dissolved to form a dark red solution. The whole was kept overnight, poured into water, and the precipitated solid fractionally crystallised from acetone slightly diluted with water, when ultimately two *tetranitrotetramethyldiphenyls* were obtained, the one crystallising in stellar aggregate of thin, transparent needles, melting at $267\text{--}268^\circ$:

0.1171 gave 14.4 c.c. N_2 (moist) at 15° and 758 mm. $\text{N}=14.36$.

$\text{C}_{16}\text{H}_{14}\text{O}_8\text{N}_4$ requires $\text{N}=14.36$ per cent.

and the second separating from acetone containing a little water in stout, prismatic needles, melting at 208—210°:

0.1265 gave 15.4 c.c. N_2 (moist) at 14° and 759 mm. $N=14.31$.

$C_{16}H_{14}O_8N_4$ requires $N=14.36$ per cent.

The nitration was also carried out with a mixture of nitric and sulphuric acids, but the reaction is evidently of a very complicated nature, and although many fractions of intermediate melting point were obtained, the above-mentioned tetranitro-derivatives were the only definite substances isolated.

Reduction of Nitrotetramethyldiphenyl.

Ten grams of nitrotetramethyldiphenyl were heated on the water-bath with tin and hydrochloric acid, with constant shaking. Reduction took place extremely slowly, owing to the insolubility of the nitro-compound, and after heating for four or five hours it was found best to filter the mixture (the filtrate deposited white needles of the hydrochloride of aminotetramethyldiphenyl on standing) and treat the solid residue with fresh quantities of tin and hydrochloric acid. This process was repeated several times, excess of sodium hydroxide solution added to the solid obtained from the last filtration, and the whole extracted six times with ether (extract = *B*). The hydrochloride mentioned above was also decomposed with sodium hydroxide, extracted with ether, and the ethereal solution added to *B*, washed with water, dried over potassium carbonate, and the ether evaporated, when 8.7 grams of a solid were obtained, in which the nitrogen was determined after crystallisation from light petroleum (b. p. 40—60°):

0.1464 gave 8.2 c.c. N_2 (moist) at 16° and 752 mm. $N=6.46$.

$C_{16}H_{19}N$ requires $N=6.22$ per cent.

Aminotetramethyldiphenyl is readily soluble in the cold in ethyl acetate, acetone, or benzene, less readily soluble in ethyl alcohol, and crystallises from light petroleum (b. p. 40—60°) in sheaves of stout, colourless, transparent needles, melting at 80°.

The *hydrochloride* which separated during the preparation of the base was purified by crystallisation from dilute hydrochloric acid:

0.2000 gave 0.1096 AgCl. $Cl=13.56$.

$C_{16}H_{19}N.HCl$ requires $Cl=13.57$ per cent.

3:4:3':4'-Tetramethyldiphenyl from Aminotetramethyldiphenyl.

Two quantities of 5 grams of the base were diazotised and treated with stannous chloride exactly as described by Morgan, Micklethwait, and Winfield (Trans., 1904, **85**, 746) for the conversion of 4-bromotetrahydro- α -naphthylamine into 1-bromotetra-

hydronaphthalene. On distilling in steam a yellowish-white solid (2 grams) passed over extremely slowly, which was extracted with ether and crystallised from alcohol:

0.2044 gave 0.6848 CO_2 and 0.1527 H_2O . $\text{C} = 91.37$; $\text{H} = 8.30$.

$\text{C}_{16}\text{H}_{18}$ requires $\text{C} = 91.43$; $\text{H} = 8.57$ per cent.

3:4:3':4'-*Tetramethyldiphenyl* is fairly readily soluble in the cold in chloroform, benzene, ethyl acetate, or acetone, very soluble on warming, and crystallises from alcohol in long, transparent, pale yellow needles, melting at $76-77^\circ$.

Synthesis of 3:4:3':4'-Tetramethyldiphenyl.

4-Nitro-*o*-xylene was reduced with tin and hydrochloric acid (Jacobson, *Ber.*, 1884, **17**, 160), and the resulting amino-*o*-xylene (m. p. 49°) diazotised in 10 per cent. sulphuric acid solution. Potassium iodide (2 grams for each gram of base), dissolved in twice its weight of water, was then slowly added, the whole allowed to remain for one hour, and then heated on the water-bath until evolution of nitrogen had ceased, when a heavy, dark-coloured oil sank to the bottom of the containing flask. The whole was shaken with sodium bisulphite solution to remove iodine, and distilled in steam, when 4-iodo-*o*-xylene passed over as a heavy, yellow oil. It boils in air with some decomposition at $228-232^\circ$.

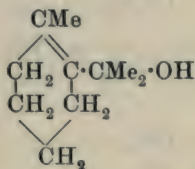
Five grams of iodoxyene were heated to $220-225^\circ$ (compare Ullmann, *Annalen*, 1904, **332**, 38), and 5 grams of copper powder gradually added. The temperature was then slowly raised to 268° , where it was maintained for twenty-five minutes. The product was a dark brown powder, which was extracted three times with ether and the filtered ethereal solution evaporated, when 0.5 gram of a solid resulted, which crystallised from alcohol in pale yellow, transparent needles, melting at 76° ; nor was this melting point altered by admixture with the tetramethyldiphenyl prepared by elimination of the nitro-group from nitrotetramethyldiphenyl.

Experiments were made on the nitration of this synthetic hydrocarbon in the hope of preparing the nitrotetramethyldiphenyl melting at 115° ; but even when nitrated at -10° the raw material melted somewhat indefinitely at $120-127^\circ$, and gave, after fractional crystallisation from acetone diluted with water, the tetra-nitrotetramethyldiphenyl melting at $267-268^\circ$, described on page 724.

LXXX.—*Experiments on the Synthesis of the Terpenes.*
 Part XVIII. *Synthesis of Δ^5 -o-Menthenol(8), Δ^6 -o-Menthenol(8), and the Corresponding Menthadienes.*

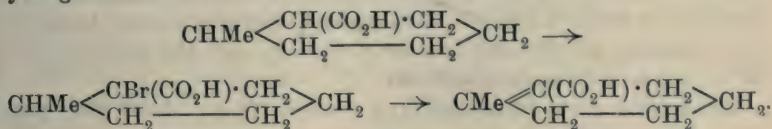
By WILLIAM HENRY PERKIN, jun.

IN Part XIV of this research (Trans., 1910, **97**, 2129) it was shown that the problem of the synthesis of those menthenols belonging to the meta-series which contain the hydroxyl group in the position (8) has been solved, since the six possible isomerides have now all been synthesised and investigated in detail. On the other hand, the only corresponding member of the ortho-series which has so far been synthesised is Δ^1 -o-menthenol(8):

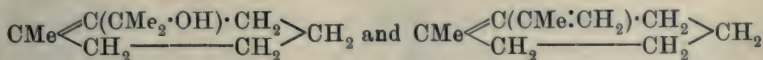


which Kay and Perkin prepared in 1905 (Trans., **87**, 1068).

The starting point in this synthesis was *o*-toluic acid, which was reduced by sodium and *iso*amyl alcohol to 1-methylcyclohexane-2-carboxylic acid, and then converted into 1-methyl- Δ^1 -cyclohexene-2-carboxylic acid by bromination and subsequent elimination of hydrogen bromide:

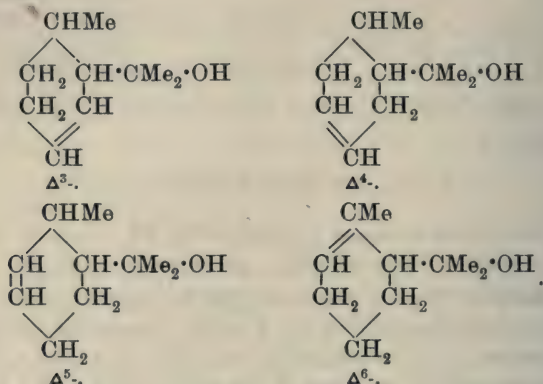


The ester of the unsaturated acid yielded, on treatment with magnesium methyl iodide, Δ^1 -o-menthenol(8), from which $\Delta^{1:8(9)}$ -o-menthadiene was obtained by dehydration with potassium hydrogen sulphate:

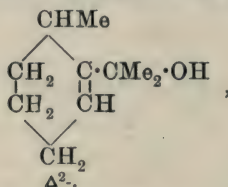


The experiments described in this and the next communication were undertaken with the object of synthesising the remaining menthenols of the ortho-series, and methods are described with the aid of which it has been found possible to prepare the following

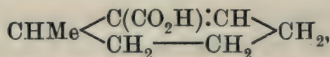
new menthenols in quantity sufficient for careful preliminary investigation :



The only remaining member of this series is, therefore :

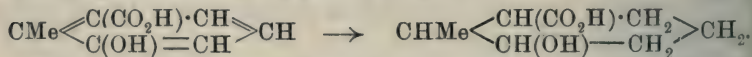


and the synthesis of this isomeride has, so far, not been possible because a method has not yet been discovered for the preparation of 1-methyl- Δ^2 -cyclohexene-2-carboxylic acid :



the ester of which should yield this menthenol on treatment with magnesium methyl iodide. The present communication deals with the synthesis of Δ^5 - and Δ^6 -*o*-menthenol(8) and the corresponding $\Delta^{5:8(9)}$ - and $\Delta^{6:8(9)}$ -*o*-menthadienes.

Some time since (Baudisch and Perkin, Trans., 1909, **95**, 1884) it was shown that 6-hydroxy-*o*-toluic acid is reduced by sodium and alcohol with the formation of the *cis*- and *trans*-modifications of 1-methylcyclohexan-6-ol-2-carboxylic acid * :

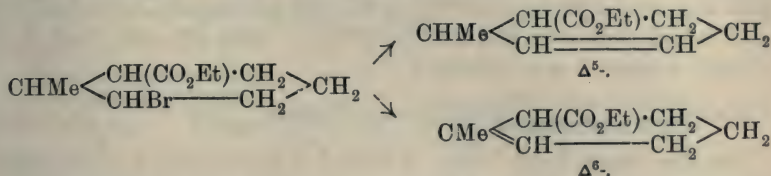


For the present research large quantities of these mixed acids were prepared and converted into the mixed 6-bromo-1-methylcyclohexan-2-carboxylic acids by the action of fuming hydrobromic acid.

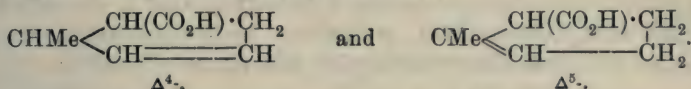
When the esters of these bromo-acids are digested with diethyl-

* Previously named 1-methylcyclohexan-2-ol-6-carboxylic acid.

aniline, hydrogen bromide is readily eliminated, and an unsaturated ester results, which investigation has shown to be a mixture of *ethyl 1-methyl- Δ^5 - and 1-methyl- Δ^6 -cyclohexenecarboxylates*:

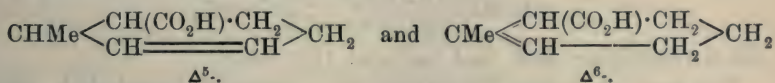


The mixed Δ^5 - and Δ^6 -acids, obtained by the hydrolysis of these esters, are liquid, and do not appear to yield characteristic salts; their separation by the fractional crystallisation of their salts was therefore found to be impossible. The only course left seemed to be the process of fractional esterification and hydrolysis which had already been adopted with success by Haworth and Perkin (*Trans.*, 1908, **93**, 577) in the case of the isomeric 1-methyl- Δ^4 - and 1-methyl- Δ^5 -cyclopentenecarboxylic acids:



Of these isomeric acids, the Δ^4 -modification esterifies more rapidly at the ordinary temperature than the Δ^5 -, and again the ester of the Δ^4 -modification is hydrolysed by methyl-alcoholic potassium hydroxide in the cold with greater ease than the ester of the Δ^5 -acid. These results seem to indicate that the grouping, $>\text{C}:\text{CMe}-$, contained in the Δ^5 -acid, has a retarding effect on the esterification of that acid and on the hydrolysis of its ester.

A comparison of the formulæ of 1-methyl- Δ^5 - and 1-methyl- Δ^6 -cyclohexene-2-carboxylic acids:

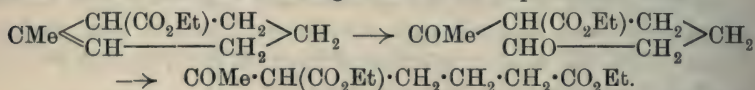


with those of the pentene acids pictured above, shows that there is great similarity in constitution, and that the essential groupings are the same and in the same positions in both series. In conformity with this view, experiment proved that 1-methyl- Δ^6 -cyclohexene-2-carboxylic acid, which contains the grouping $>\text{C}:\text{CMe}-$, does actually esterify less readily than 1-methyl- Δ^5 -cyclohexene-2-carboxylic acid, and that its ester is less readily hydrolysed than the ester of the Δ^5 -acid. By repeating the process of fractional esterification and hydrolysis a great number of times, what is believed to be an almost complete separation of these acids was ultimately accomplished.

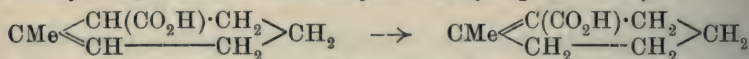
The constitution of 1-methyl- Δ^5 -cyclohexene-2-carboxylic acid was controlled by oxidation, first with ozone, and then with permanganate, when an acid was obtained which melted at 177—178°, and was found to be identical with the pentane- $\beta\gamma$ -tricarboxylic acid which Haworth and Perkin (Trans., 1908, **93**, 581) had previously prepared synthetically:



On the other hand, ethyl 1-methyl- Δ^6 -cyclohexene-2-carboxylate is converted, by oxidation with ozone, into an aldehydo-ester, which, on further oxidation with chromic acid and subsequent esterification, yields a ketonic ester the alcoholic solution of which gives a violet coloration on the addition of ferric chloride. There can be no doubt that these changes are to be represented thus:

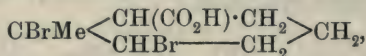


Again, 1-methyl- Δ^6 -cyclohexene-2-carboxylic acid is converted, by boiling with concentrated potassium hydroxide solution, into 1-methyl- Δ^1 -cyclohexene-2-carboxylic acid (m. p. 87—88°):



a change which is well known to be characteristic of acids in which the double linking occupies the $\beta\gamma$ -position. The conversion, in this case, appears to be only partial, and it is probable that an equilibrium mixture of the two isomerides is produced.

1-Methyl- Δ^6 -cyclohexene-2-carboxylic acid is further characterised by the fact that it combines readily with bromine to form 1:6-dibromo-1-methylcyclohexane-2-carboxylic acid,

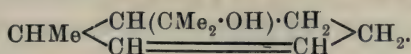
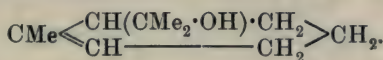
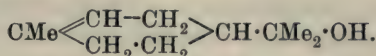


which crystallises well, and melts at 160—162°.

The next step was to convert the esters of 1-methyl- Δ^5 - and 1-methyl- Δ^6 -cyclohexene-2-carboxylic acids into the corresponding menthenols by means of magnesium methyl iodide, and then into the menthadienes, which are readily produced from the menthenols, either by shaking with 5 per cent. sulphuric acid in the cold, or by boiling with 6 per cent. oxalic acid.

The properties of these new *o*-menthenols and *o*-menthadienes may be conveniently tabulated and compared with those of α -terpineol and limonene.

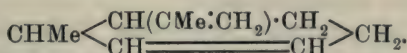
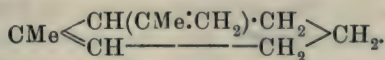
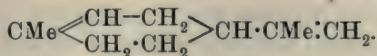
TABLE I.

I. Δ^5 -*o*-Menthenol(8),II. Δ^6 -*o*-Menthenol(8),III. Δ^1 -*p*-Menthenol(8), or α -terpineol,

	I.	II.	III.
Boiling point... ..	110—112°/30 mm. (198—200°/734 mm.)	107—108°/30 mm.	218°
d_{20}	0.9404	0.9412	0.938
n_D	1.4792	1.4811	1.4820
M.....	46.6 (Cal. 47.16)	46.8	46.8

With the exception of the boiling points, which are approximately 15—20° lower, it will be seen that the properties of these *o*-menthenols are very similar to those of α -terpineol.

TABLE II.

I. $\Delta^{5:8(9)}$ -*o*-Menthadiene,II. $\Delta^{6:8(9)}$ -*o*-Menthadiene,III. $\Delta^{1:8(9)}$ -*p*-Menthadiene or limonene,

	I.	II.	III.
Boiling point	170—171°	170—171°	176°
d_{20}	0.8490	0.8481	0.846
n_D	1.4778	1.4758	1.4746
M	45.24	45.2	45.23

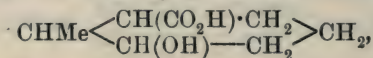
Calculated for $\text{C}_{10}\text{H}_{16}$ \bar{f}^2 45.24.

In this comparison, again, the most striking fact is the low boiling points of the *o*-menthadienes.

EXPERIMENTAL.

Preparation and Separation of 1-Methyl- Δ^5 -cyclohexene-2-carboxylic Acid and 1-Methyl- Δ^6 -cyclohexene-2-carboxylic Acid.

In the preparation of these acids, the mixture of the *cis*- and *trans*-modifications of 1-methylcyclohexan-6-ol-2-carboxylic acid,*



obtained by the reduction of 6-hydroxy-*o*-toluic acid, as described in the previous communication (Trans., 1909, **95**, 1885), in quantities of 50 grams, was mixed with twice its volume of fuming hydrobromic acid (saturated at 0°), and, after remaining overnight, heated on the water-bath for two hours. The cold product was diluted with water, extracted with ether, the ethereal solution dried, evaporated, and the residual crude 6-bromo-1-methylcyclohexane-2-carboxylic acid esterified by digesting with a large excess of 15 per cent. alcoholic sulphuric acid for five hours on the water-bath. After adding water and extracting with ether, the ethereal solution was well washed with sodium carbonate (which removed much dark-coloured impurity), carefully dried, evaporated, and the residue boiled with four times its volume of diethylaniline for six hours; it was then allowed to cool, mixed with excess of dilute hydrochloric acid, and the unsaturated esters extracted with ether and distilled in a current of steam.

The residue in the steam distillation flask was extracted with ether, and again treated with hydrobromic acid and diethylaniline exactly as before, when a further considerable yield of unsaturated esters was obtained. The combined esters, on fractionating under diminished pressure, distilled for the most part at 135–145°/100 mm., and consisted essentially of unsaturated esters of the formula $\text{C}_{10}\text{H}_{16}\text{O}_2$, as the analysis showed. (Found, C=70.9; H=9.5. $\text{C}_{10}\text{H}_{16}\text{O}_2$ requires C=71.4; H=9.5 per cent.) In hydrolysing this ester, care was taken at this and all subsequent stages not to heat with potassium hydroxide, so as to avoid, as far as possible, any tendency to molecular change due to the wandering of the double linking in the direction of the carboxyl group. Some of the ester was completely hydrolysed by leaving it with a large excess of methyl-alcoholic potassium hydroxide at the ordinary temperature for several days; the product was nearly neutralised, saturated with carbon dioxide, and evaporated until free from methyl alcohol. After acidifying, the mixed acids were extracted with ether, the ethereal solution dried, evaporated, and

* Previously named 1-methylcyclohexan-2-ol-6-carboxylic acid (*loc. cit.*).

the residue distilled, when almost the whole passed over at 182—183°/100 mm., and, on analysis, gave numbers agreeing with the formula $C_8H_{12}O_2$.

This mixture of 1-methyl- Δ^5 - and - Δ^6 -cyclohexene-2-carboxylic acids was next converted into the calcium, barium, and other salts in order to see whether any of these crystallised well and were suitable for the separation of the isomerides, but no suitable salt could be found. The acids were also fractionally distilled in a current of steam, and the fractions kept at 0° in order, if possible, to freeze out one of the constituents, but these experiments were also without useful result.

Subsequently it was discovered that one of the isomerides esterified more rapidly than the other, and a process of fractional esterification based on this observation resulted ultimately in the separation of the isomerides. The detailed description of this process would take up too much space and is unnecessary, since the method will be readily followed from the description of one or two of the stages. The total quantity of crude unsaturated ester available was 490 grams, and this was worked up in two exactly parallel experiments. The ester (245 grams) was mixed with a cold solution of potassium hydroxide (120 grams) in methyl alcohol (400 grams) and water (20 c.c.), and, after remaining for three days at the ordinary temperature, water was added, and the unhydrolysed ester (A, 50 grams) extracted with ether. The aqueous solution was acidified, extracted with ether, the ethereal solution washed, dried, evaporated, and the residual acid mixed with alcohol (600 c.c.) and sulphuric acid (50 c.c.) in the cold, and left for twenty-four hours at the ordinary temperature. The product was diluted with water, extracted with ether, the ethereal solution thoroughly washed with sodium carbonate, and the unchanged acid regenerated from the sodium carbonate solution; the quantities obtained as the result of this treatment were 110 grams of ester (B) and 100 grams of acid (C). The acid (C), which had escaped esterification, was esterified by boiling with alcohol (400 c.c.) and sulphuric acid (25 c.c.) on the water-bath, and the ester, after extracting in the usual manner, again fractionally hydrolysed with cold methyl-alcoholic potassium hydroxide. After repeating this process a very large number of times, and systematically working up the intermediate fractions, an operation which occupied several months, the following products were ultimately isolated:

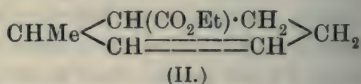
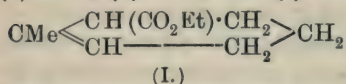
I. An ester (73 grams), which is hydrolysed with comparative difficulty, and the acid corresponding with which does not esterify readily at the ordinary temperature. This is the *ester of 1-methyl- Δ^6 -cyclohexene-2-carboxylic acid*.

II. An ester (52 grams), which is more readily hydrolysed, and the acid of which is more readily esterified. This is the *ester of 1-methyl- Δ^5 -cyclohexene-2-carboxylic acid*.

When these esters had been separated, it was thought interesting to make roughly comparative experiments with the view to obtaining some idea of their relative rates of hydrolysis. In each experiment, the ester (1 gram) was dissolved in methyl alcohol (1 c.c.) and mixed with 5 c.c. of methyl-alcoholic potassium hydroxide (containing 0.1134 gram of KOH in each c.c.), and, after remaining for forty-eight hours at the ordinary temperature, water was added, and the excess of alkali determined by titration with *N*/10-hydrochloric acid. Three pairs of experiments were made with three different preparations under exactly the same conditions, and the amount of the esters which had been hydrolysed were found to be the following:

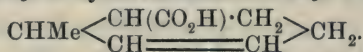
In the case of ethyl 1-methyl- Δ^6 -cyclohexene-2-carboxylate (I), (*a*)=42; (*b*)=39; and (*c*)=43 per cent.

In the case of ethyl 1-methyl- Δ^5 -cyclohexene-2-carboxylate (II), (*a*)=64; (*b*)=66; and (*c*)=70 per cent.



These experiments are, of course, very rough, but they are sufficiently accurate to show that the relative rates of hydrolysis of the esters vary sufficiently to allow of an almost complete separation by the process of fractional esterification adopted. At the same time, it is clear from the nature of the separation that, whilst the ester of the Δ^6 -acid was probably entirely free from that of the Δ^5 -acid, the ester of the Δ^5 -acid probably still contained traces of that of the Δ^6 -acid.

1-Methyl- Δ^5 -cyclohexene-2-carboxylic Acid,



This acid was obtained from the ester (II, see above) by hydrolysis with methyl-alcoholic potassium hydroxide in the cold. The product was diluted with water, a trace of unhydrolysed ester removed by ether, the aqueous solution was then saturated with carbon dioxide, and evaporated until free from methyl alcohol. After acidifying with dilute hydrochloric acid, the acid was extracted with pure ether, the extract dried thoroughly, and distilled:

0.1919 gave 0.4815 CO_2 and 0.1505 H_2O . C=68.4; H=8.7.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires C=68.6; H=8.6 per cent.

1-Methyl- Δ^5 -cyclohexene-2-carboxylic acid is a viscid oil, which distils at $139^\circ/20$ mm., and did not crystallise; its solution in sodium carbonate instantly decolorises permanganate.

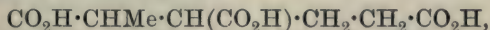
Ethyl 1-methyl- Δ^5 -cyclohexene-2-carboxylate.—This ester was prepared by leaving the pure acid (40 grams) in contact with alcohol (200 c.c.) and sulphuric acid (15 c.c.) for three days at the ordinary temperature. The product was diluted with water, extracted with ether, the ethereal solution carefully washed with sodium carbonate, dried, evaporated, and the ester distilled:

0.1116 gave 0.2914 CO_2 and 0.0973 H_2O . $\text{C}=71.2$; $\text{H}=9.7$.

$\text{C}_{10}\text{H}_{16}\text{O}_2$ requires $\text{C}=71.4$; $\text{H}=9.5$ per cent.

This ester distils at $138\text{--}139^\circ/100$ mm., and has a most penetrating and unpleasant odour.

Oxidation of 1-Methyl- Δ^5 -cyclohexene-2-carboxylic Acid to Pentane- $\beta\gamma\epsilon$ -tricarboxylic Acid,



by means of Ozone and Permanganate.—In carrying out this oxidation, the acid (5 grams) was dissolved in a slight excess of dilute sodium carbonate, made up to 50 c.c. with water, and a current of ozonised oxygen passed for about two days and until it escaped freely. The solution was mixed with much powdered ice, and then permanganate (1 per cent.) added until the colour remained permanent, the whole being vigorously stirred by a turbine during the operation.

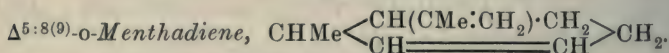
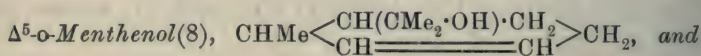
The product was heated on the water-bath, filtered, the filtrate and washings of the manganese precipitate rendered acid to Congo paper with dilute hydrochloric acid, evaporated to dryness, and the residue mixed with sand and extracted with ether in a Soxhlet apparatus.

After the ether had been removed, the brown, syrupy extract was esterified by boiling with alcohol (50 c.c.) and sulphuric acid (5 c.c.) in a reflux apparatus for two days, water was then added, and the ester extracted with ether. The ethereal solution was thoroughly washed with dilute sodium carbonate, dried, evaporated, and the ester distilled, when, with the exception of a small quantity of oil boiling at about $120^\circ/20$ mm., nearly the whole distilled at $183\text{--}185^\circ/20$ mm., and consisted of ethyl pentane- $\beta\gamma\epsilon$ -tricarboxylate. (Found, $\text{C}=58.2$; $\text{H}=8.5$. Calc., $\text{C}=58.3$; $\text{H}=8.3$ per cent.)

This ester was boiled with dilute hydrochloric acid (1 vol. conc. acid and 2 vols. of water) for six hours, and the solution evaporated to a small bulk, and placed over solid potassium hydroxide in a vacuum desiccator, when it gradually crystallised. The semi-solid

mass was drained on porous porcelain, and the residue crystallised from hydrochloric acid, from which it separated as a crust, which melted at 177—178°, and consisted of pure pentane- $\beta\gamma\epsilon$ -tricarboxylic acid. (Found, C=46·8; H=6·1. Calc., C=47·1; H=5·9 per cent.)

On titration with $N/10$ -NaOH, 0·2918 required 42·4 c.c. for neutralisation, whereas this amount of a tribasic acid, $C_8H_{12}O_6$, neutralises 42·8 c.c. The identity of the acid was further proved by mixing it with a specimen of pentane- $\beta\gamma\epsilon$ -tricarboxylic acid which had previously been prepared synthetically (Trans., 1908, 93, 580), when the mixture melted at the same temperature as the constituents.



The former of these substances was readily obtained when ethyl 1-methyl- Δ^5 -cyclohexene-2-carboxylate (26 grams) was added to an ethereal solution of magnesium methyl iodide (containing 11 grams of magnesium). After two days, the product was decomposed by water and dilute hydrochloric acid, the ethereal solution evaporated, and the residue mixed with methyl-alcoholic potassium hydroxide (KOH=5 grams), and left for three days at the ordinary temperature. Water was then added, the oil extracted with ether, the ethereal solution thoroughly washed, dried over anhydrous sodium sulphate, and evaporated.

The residual oil distilled at 110—112°/30 mm., or at about 140°/100 mm.:

0·1400 gave 0·3984 CO_2 and 0·1449 H_2O . C=77·6; H=11·5.

$C_{10}H_{18}O$ requires C=77·9; H=11·7 per cent.

$\Delta^5\text{-o-Menthenol(8)}$ is a rather viscid, colourless syrup, with a pronounced odour of terpineol, and distils apparently with very little decomposition at 198—200°/734 mm. Its solution in acetic anhydride gives, on the addition of a drop of sulphuric acid, a pale pink coloration. The determination of its density and refractive index gave the following values: $d_{20/20^\circ}=0\cdot9404$; $n_D=1\cdot4792$; $M=46\cdot6$ (calc., 47·16).

The *phenylurethane*.—This derivative was prepared by sealing up the menthenol with an equal volume of phenylcarbimide. After several days, the crystalline mass was mixed with a little light petroleum, drained on porous porcelain, and recrystallised from dilute methyl alcohol, in which it is readily soluble, and from which it separates in slender needles, melting at 118—119°:

0.1997 gave 9.7 c.c. N_2 at 18° and 752 mm. $N=5.5$.

$C_{17}H_{23}O_2N$ requires $N=5.1$ per cent.

An attempt to prepare a crystalline nitroso-chloride was unsuccessful.

$\Delta^{5:8(9)}$ -*o*-Menthadiene.—This terpene was first obtained in an attempt to prepare the corresponding terpin from Δ^5 -*o*-menthenol(8) by the action of cold dilute sulphuric acid. The menthenol (5 c.c.) was shaken for six days with 5 per cent. sulphuric acid (250 c.c.), a second 250 c.c. of the acid was then added, and the shaking continued for a further six days. During this operation it was noticed that the viscid oil, which at first largely dissolved, became more mobile and insoluble. The product was neutralised with sodium carbonate, distilled in a current of steam, the distillate extracted with ether, the ethereal solution dried, evaporated, and the residue distilled, when almost the whole quantity passed over at 170 — 175° , and, after twice fractionating over sodium, the $\Delta^{5:8(9)}$ -*o*-menthadiene distilled at 170 — 171° :

0.1491 gave 0.4789 CO_2 and 0.1065 H_2O . $C=87.7$; $H=12.0$.

$C_{10}H_{16}$ requires $C=88.2$; $H=11.8$ per cent.

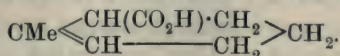
The residue in the steam distillation flask yielded, on extraction, only a trace of a syrup, showing that practically no terpin is produced under the above conditions.

Subsequently a larger quantity of $\Delta^{5:8(9)}$ -*o*-menthadiene was prepared by boiling Δ^5 -*o*-menthenol(8) with 6 per cent. aqueous oxalic acid in a reflux apparatus for five hours. The product was distilled in a current of steam, and the terpene repeatedly fractionated over sodium, when it boiled constantly at 170 — $171^\circ/765$ mm.

The physical properties were determined, with the following results: $d_{17/17^\circ}=0.8490$; $n_D=1.4778$; $M=45.24$ (calc., 45.24).

When the terpene (1 gram), dissolved in chloroform (5 c.c.), was cooled to -10° and titrated with a 10 per cent. solution of bromine in chloroform, it absorbed 2.2 grams of bromine, whereas the amount required for the formation of the additive compound, $C_{10}H_{16}Br_4$, is 2.36 grams. After removing the chloroform by a current of dry air, a colourless syrup remained, which did not crystallise, and soon became dark coloured.

1-Methyl- Δ^6 -cyclohexene-2-carboxylic Acid,



Careful examination of the ester of this acid (I, p. 733) showed that, although it was free from the ester of the Δ^5 -acid, it contained about 2 per cent. of the ester of an acid, which is esterified with

still greater difficulty than 1-methyl- Δ^6 -cyclohexene-2-carboxylic acid, and which, on investigation, proved to be *o*-toluic acid (compare p. 745).

In order to remove this slight impurity, the ester was mixed with a large excess of methyl-alcoholic potassium hydroxide, and left until completely hydrolysed. The acid was then isolated, mixed with excess of methyl-alcoholic sulphuric acid, and, after about a week, the ester was extracted, washed with sodium carbonate (which dissolves crude *o*-toluic acid), and again subjected three times to the same process, after which no further separation of solid *o*-toluic acid could be observed. A portion of the purified ester was hydrolysed, and the 1-methyl- Δ^6 -cyclohexene-2-carboxylic acid fractionated, when the whole quantity passed over at 140—142°/20 mm. as a colourless syrup which did not crystallise:

0.1928 gave 0.4836 CO₂ and 0.1516 H₂O. C=68.4; H=8.7.

C₈H₁₂O₂ requires C=68.6; H=8.6 per cent.

1:6-Dibromo-1-methylcyclohexane-2-carboxylic Acid.—This dibromo-acid was prepared by adding dry bromine to the solution of 1-methyl- Δ^6 -cyclohexene-2-carboxylic acid in chloroform at -10°, when it was found that 1.1 grams of the acid absorbed 1.2 grams of bromine (calc., 1.25) readily and without evolution of hydrogen bromide. The chloroform was removed by aspirating a current of dry air through the solution, and the gum left for several days over sulphuric acid and paraffin wax in a desiccator, when it gradually crystallised. The almost solid mass was rubbed with a few drops of formic acid, left in contact with porous porcelain until quite dry, and then crystallised from warm formic acid, in which it is readily soluble:

0.1632 gave 0.2035 AgBr. Br=53.0.

C₈H₁₂O₂Br requires Br=53.3 per cent.

This dibromo-acid softens at 155°, and melts at 160—162°; it is readily soluble in dilute sodium carbonate, and, when the solution is boiled, it clouds, and an oil separates which has the odour of a bromo-hydrocarbon.

Oxidation of Ethyl 1-Methyl- Δ^6 -cyclohexene-2-carboxylate with Ozone.—In this experiment the ester (10 grams) was dissolved in chloroform (40 c.c.), the solution placed in a narrow cylinder, covered with water (20 c.c.), and then a stream of ozonised oxygen passed for several days and until it escaped freely, the chloroform and water being renewed as they evaporated. The solution was separated from the water, washed, dried, and the chloroform evaporated at a low temperature, when a colourless, viscid syrup remained, which had an odour like heptaldehyde and doubtless con-

sisted of the aldehyde-ester, $\text{COMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$. After remaining over sulphuric acid in a vacuum desiccator for two days, the following analysis was made:

0.1411 gave 0.3074 CO_2 and 0.1053 H_2O . $\text{C}=59.4$; $\text{H}=8.3$.

$\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C}=60.0$; $\text{H}=8.0$ per cent.

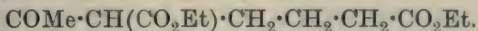
The syrup (10 grams) was dissolved in glacial acetic acid, water was added until the turbidity just redissolved, and the solution was then gradually mixed with chromic acid (4 grams) in a little water, the temperature being kept below 40° . When all the chromic acid had been added, the liquid was heated for half an hour on the steam-bath, and then mixed with 100 c.c. of 10 per cent. alcoholic sulphuric acid and gently boiled in an open flask for six hours, small quantities of alcohol being added from time to time. The product was diluted with water, extracted with ether, the ethereal solution washed with water and sodium carbonate, evaporated, and the residue distilled under diminished pressure.

After a small quantity had passed over at $120\text{--}140^\circ/30$ mm., the residue distilled at $180\text{--}182^\circ/25$ mm. as a pale yellow oil:

0.1231 gave 0.2652 CO_2 and 0.0909 H_2O . $\text{C}=58.5$; $\text{H}=8.2$.

$\text{C}_{12}\text{H}_{20}\text{O}_5$ requires $\text{C}=59.0$; $\text{H}=8.2$ per cent.

Since this ester gave a violet coloration when ferric chloride was added to its alcoholic solution and a green copper salt when it was shaken with ammoniacal copper sulphate, there can be little doubt that it is ethyl α -acetyladipate,



This ester had already been obtained in small quantity by Fichter and Gully (*Ber.*, 1897, **30**, 2047) from ethyl γ -chlorobutyrate and the potassium derivative of ethyl acetoacetate. They state that it yields δ -acetylvaleric acid, $\text{COMe}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$, on hydrolysis with acids, but the boiling point which they give for their ester, $160^\circ/12$ mm., is considerably lower than that found for the ester described above. The available ester (4 grams) was digested with 1 per cent. hydrochloric acid for four hours, and the solution saturated with ammonium sulphate and extracted with ether, when a syrup was obtained which was insufficient for distillation, but, since it gave a copious precipitate of bromoform with bromine and sodium hydroxide, it very probably consisted of δ -acetylvaleric acid.

Conversion of 1-Methyl- Δ^5 -cyclohexene-2-carboxylic Acid into 1-Methyl- Δ^1 -cyclohexene-2-carboxylic Acid by the Action of Potassium Hydroxide.—This intramolecular change was brought about by boiling the first-mentioned acid with 15 per cent. potassium hydroxide for six hours. The resulting mixture of acids was left

in contact with 5 per cent. alcoholic sulphuric acid for twenty-four hours, extracted with ether, and the unesterified acid removed by sodium carbonate.

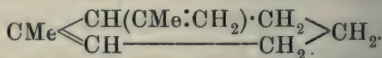
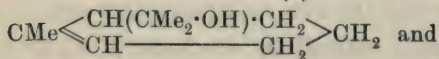
On acidifying the sodium carbonate solution, the acid showed no signs of crystallising, but, after the partial esterification had been repeated, an acid was obtained which, after distillation in a current of steam, became semi-solid. In contact with porous porcelain the oily impurity was soon absorbed, and the residue crystallised from a little formic acid in starry aggregates:

0.1073 gave 0.2709 CO_2 and 0.0851 H_2O . $\text{C} = 68.8$; $\text{H} = 8.8$.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires $\text{C} = 68.6$; $\text{H} = 8.8$ per cent.

This acid melted at $87-88^\circ$, and was identified as 1-methyl- Δ^1 -cyclohexene-2-carboxylic acid by the fact that the admixture with a specimen of this acid which had been prepared by Kay and Perkin (Trans., 1905, **87**, 1074) melted at $86-88^\circ$.

Δ^6 -o-Menthenol(8) and $\Delta^{6:8(9)}$ -o-Menthadiene.



In preparing Δ^6 -o-menthenol(8), ethyl 1-methyl- Δ^6 -cyclohexene-2-carboxylate (30 grams) was added to an ethereal solution of magnesium methyl iodide containing 14 grams of magnesium, and, after remaining for twenty-four hours, the product was decomposed by water and dilute hydrochloric acid in the usual way. The ethereal solution was evaporated, and any possible trace of unchanged ester removed by leaving the oil with methyl-alcoholic potassium hydroxide (5 grams) for three days.

Water was then added, the oil extracted with ether, the ethereal solution washed well, dried over anhydrous sodium sulphate, evaporated, and the residue fractionated, when almost the whole quantity distilled at $107-108^\circ/30$ mm., little, if any, of the corresponding menthadiene having been produced (compare footnote, Trans., 1910, **97**, 2154):

0.1547 gave 0.4401 CO_2 and 0.1615 H_2O . $\text{C} = 77.6$; $\text{H} = 11.6$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C} = 77.9$; $\text{H} = 11.7$ per cent.

$d_{20/20^\circ}$ 0.9412; n_D 1.4811; M 46.8 (calc., 47.16).

Δ^6 -o-Menthenol(8) is a viscid oil with a pronounced odour reminiscent of terpineol and menthol; it distils, apparently with little decomposition, at $200-202^\circ/734$ mm., and its solution in acetic anhydride gives with a drop of sulphuric acid an orange-brown coloration.

Attempts to prepare the phenylurethane and nitrosochloride in a crystalline condition were unsuccessful.

$\Delta^{6:8(9)}$ -*o*-Menthadiene.—This terpene was prepared by digesting Δ^6 -*o*-menthenol(8) with 5 per cent. oxalic acid for six hours, and then distilling in a current of steam. After extracting with ether, the ethereal solution was dried, evaporated, and the residue several times distilled over sodium:

0.1497 gave 0.4822 CO_2 and 0.1615 H_2O . $\text{C}=87.9$; $\text{H}=11.9$.

$\text{C}_{10}\text{H}_{16}$ requires $\text{C}=88.2$; $\text{H}=11.8$ per cent.

$\Delta^{6:8(9)}$ -*o*-Menthadiene distils at $170\text{--}171^\circ$, and has a pungent odour of lemons and eucalyptus. The following constants were determined:

$d_{20/20^\circ} 0.8481$; $n_D 1.4758$; $M 45.2$ (calc., $\text{C}_{10}\text{H}_{16} \mid \overline{= 45.24}$).

This terpene was also prepared by shaking Δ^6 -*o*-menthenol(8) with 6 per cent. sulphuric acid mechanically for several days, when it was found that the menthenol had been almost entirely decomposed, and the terpene distilled at $170\text{--}171^\circ/765$ mm. and had $n_D 1.4766$.

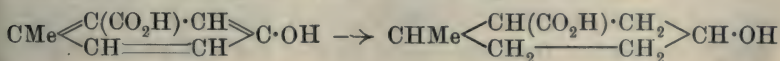
The author wishes to thank Miss B. Dobson and Mr. L. Benson for valuable assistance in carrying out these experiments, the cost of which was largely covered by generous grants from the Research Funds of the Royal Society and Chemical Society.

THE UNIVERSITY,
MANCHESTER.

LXXXI.—*Experiments on the Synthesis of the Terpenes.* *Part XIX. Synthesis of cis- and trans- Δ^3 -o-Menthenol(8), Δ^4 -o-Menthenol(8), and the Corresponding Menthadienes.*

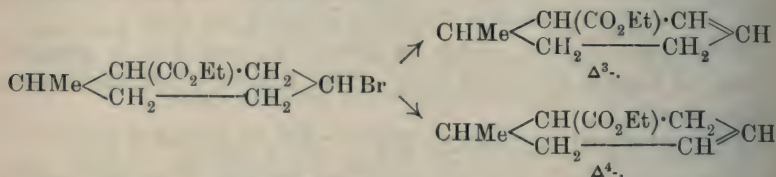
By WILLIAM HENRY PERKIN, jun.

IN a communication published a short time since (Baudisch, Hibbert, and Perkin, *Trans.*, 1909, **95**, 1873), experiments on the reduction of 4-hydroxy-*o*-toluic acid are described which show that, when this acid is reduced by sodium and alcohol, it yields a mixture of acids from which all four possible isomerides (two *cis*- and two *trans*-) of 1-methylcyclohexan-4-ol-2-carboxylic acid:



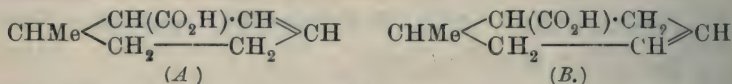
were isolated in a pure condition. For the purpose of the present

investigation large quantities of 4-hydroxy-*o*-toluic acid were reduced, and the hydroxy-acids converted into the bromo-acids by heating with fuming hydrobromic acid. The mixed bromo-acids were then esterified, and the esters digested with diethylaniline, when hydrogen bromide was readily eliminated, and the product yielded, on distillation in a current of steam, an oil which consists essentially of the mixed esters of 1-methyl- Δ^3 - and 1-methyl- Δ^4 -cyclohexene-2-carboxylic acids:



The separation of the oily mixture of the Δ^3 - and Δ^4 -acids which results from the hydrolysis of their esters, presents the same difficulty that was met with in the case of the separation of the 1-methyl- Δ^5 - and 1-methyl- Δ^6 -cyclohexene-2-carboxylic acids described in the preceding communication. All attempts to obtain salts of these Δ^3 - and Δ^4 -acids which were suitable for fractional crystallisation were unsuccessful, and the only process which was available for separation was, in this case also, fractional esterification and hydrolysis. When the mixed esters are submitted to this process a gradual separation takes place, and, after repeating it a great number of times in the manner described in the previous communication (p. 733), two esters were isolated which had very different properties, and these were hydrolysed to the corresponding acids.

The acid (A) which was the more difficult to esterify and the ester of which is hydrolysed with less readiness is 1-methyl- Δ^3 -cyclohexene-2-carboxylic acid:



whilst the acid (B), which esterifies with greater ease and the ester of which is more readily hydrolysed, is 1-methyl- Δ^4 -cyclohexene-2-carboxylic acid.

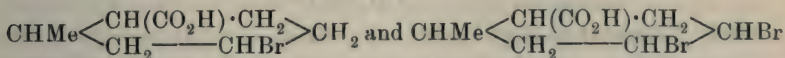
Careful investigation of the Δ^3 -acid showed that it is a mixture of *cis*- and *trans*-isomerides, of which the former is liquid and the latter crystalline (m. p. 60—62°).^{*} These were separated partly by freezing and partly by taking advantage of the fact that the *trans*-acid is somewhat less readily esterified than the *cis*-acid. The crystalline *trans*-acid was readily obtained pure, but it is probable that its separation from the liquid *cis*-acid was not quite complete,

^{*} Compare footnote p. 744.

and that the *cis*-acid contained, therefore, traces of the *trans*-modification.

Of all these isomeric acids the one which has been most completely investigated is 1-methyl- Δ^4 -cyclohexene-2-carboxylic acid.

This acid distils at 135°/12 mm., and is a colourless oil which shows no signs of crystallising; it is characterised by the fact that it combines with hydrogen bromide to form 5-bromo-1-methylcyclohexane-2-carboxylic acid (m. p. 134°), and absorbs bromine with the formation of 4:5-dibromo-1-methylcyclohexane-2-carboxylic acid (m. p. 150°):

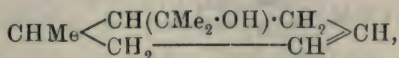


The position of the double linking of 1-methyl- Δ^4 -cyclohexene-2-carboxylic acid was demonstrated by oxidation with ozone, followed by permanganate and chromic acid, when it yielded γ -methylbutane- $\alpha\beta\delta$ -tricarboxylic acid (m. p. 153°):



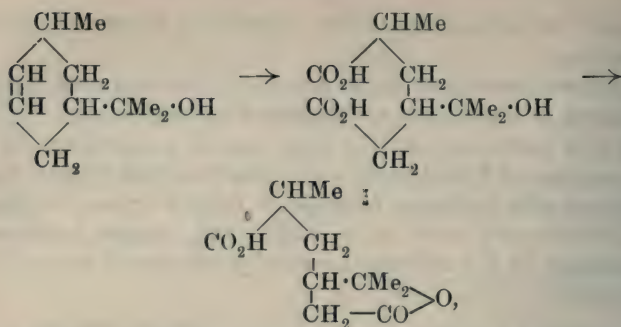
As this acid had not previously been prepared, it was synthesised for the purpose of direct comparison by a method which leaves no doubt as to its constitution (compare p. 762), and it was found that the mixture of the synthetical acid (m. p. 153—154°) with that obtained in the above oxidation melted at 153°, and, as the acids had other properties in common, there can be no doubt as to their identity.

The next step was to treat the ester of 1-methyl- Δ^4 -cyclohexene-2-carboxylic acid with magnesium methyl iodide, when the usual reaction took place readily, and the Δ^4 -*o*-menthenol(8),

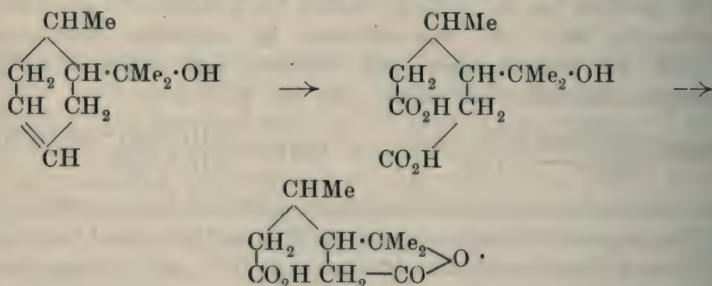


thus produced is a viscid oil with an odour of peppermint, which distils at 110°/30 mm., and yields a *phenylurethane* melting at 120°.

The constitution of this menthenol was controlled by oxidation with permanganate, and the result showed that the course of the oxidation is very similar to that which had been observed in the case of Δ^5 -*m*-menthenol(8) (Trans., 1910, 97, 2132), which contains, indeed, the double linking and the $\cdot\text{CMe}_2 \cdot \text{OH}$ group in the same relative positions as in Δ^4 -*o*-menthenol(8). Δ^5 -*m*-Menthenol(8) is oxidised by permanganate with formation of the lactone of α -methyl- γ -hydroxyisopropyladipic acid:

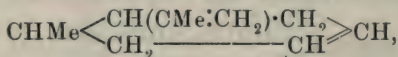


whilst Δ^4 -*o*-menthenol(8), under the same conditions, yields the lactone of β -methyl- γ -hydroxyisopropyladipic acid (m. p. 114°):



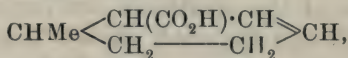
The formation of this lactonic acid is valuable evidence that the double linking in Δ^4 -*o*-menthenol(8) occupies the position assigned to it, because Δ^3 -*o*-menthenol(8), for example, could hardly give rise to a lactonic acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, on oxidation.

Δ^4 -*o*-Menthenol(8) is converted by contact with dilute sulphuric acid at the ordinary temperature into $\Delta^{4:8(9)}$ -*o*-menthadiene,



which distils at 170 — 171° , and combines with 4 atoms of bromine.

The evidence in support of the position of the double linking in the *cis*- and *trans*-acids (p. 742), to which the constitution 1-methyl- Δ^3 -cyclohexene-2-carboxylic acid,



has been assigned, is, largely owing to the relatively small quantities of material available, not quite so satisfactory * as in the case of the

* This result is not quite satisfactory, because it was not possible, on account of the small amount of material available, to oxidise each of the *cis*- and *trans*-modifications separately.

Attention should therefore be drawn to the possibility that the acid melting at 60 — 62° may prove to be 1-methyl- Δ^2 -cyclohexene-2-carboxylic acid produced

Δ^4 -acid and its derivatives. The mixture of the *cis*- and *trans*-isomerides yielded, on oxidation with ozone followed by permanganate, a syrupy acid, from which small quantities of β -methyladipic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (m. p. 84°), were ultimately isolated.

This evidence of the position of the double linking, taken in conjunction with the fact that the acids are isomeric with the Δ^4 -acid, leaves little doubt that they are the *cis*- and *trans*-modifications of 1-methyl- Δ^3 -cyclohexene-2-carboxylic acid.

The esters of these acids were converted, by the action of magnesium methyl iodide, and subsequent dehydration, into the corresponding menthenols and menthadienes, and such of the properties of these as were determined may be briefly summarised thus:

trans- Δ^3 -*o*-Menthenol(8), $\text{CHMe}\begin{array}{c} \text{CH}(\text{CMe}_2\cdot\text{OH})\cdot\text{CH} \\ \text{CH}_2\text{-----CH}_2 \end{array}\text{CH}$, boils at $110^\circ/30$ mm.

trans- Δ^3 : $8^{(9)}$ -*o*-Menthadiene, $\text{CHMe}\begin{array}{c} \text{CH}(\text{CMe}\cdot\text{CH}_2)\cdot\text{CH} \\ \text{CH}_2\text{-----CH}_2 \end{array}\text{CH}$, has b. p. $170^\circ/760$ mm., d $20/20^\circ$ 0.8477; n_D 1.4749; M 45.1, calc. $\text{C}_{10}\text{H}_{16}$, $|\text{F}|^{25} 45.24$.

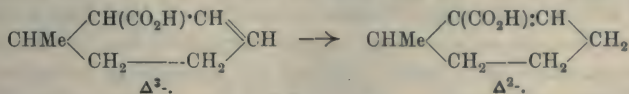
cis- Δ^3 -*o*-Menthenol(8) boils at $107\text{--}108^\circ/30$ mm.

cis- Δ^3 : $8^{(9)}$ -*o*-Menthadiene boils at $168\text{--}170^\circ/762$ mm., and has d $20/20^\circ$ 0.8507; n_D 1.4825; M 46.5, calc. $\text{C}_{10}\text{H}_{16}$, $|\text{F}|^{25} 45.24$.

Compared with limonene, which has b. p. 176° , d 0.846, and n_D 1.4746, the most striking difference in properties is the much lower boiling points of the *o*-menthadienes.

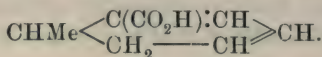
During the reduction of 4-hydroxy-*o*-toluic acid and subsequent purification of the product, small quantities of crystalline acids are obtained, and examination (p. 758) has shown that these consist of *trans*-1-methyl- Δ^3 -cyclohexene-2-carboxylic acid, *o*-toluic acid, as well as of a new acid, $\text{C}_8\text{H}_{10}\text{O}_2$, which melts at 128° . The latter acid is interesting because it is the first representative of the dihydro-*o*-toluic acids, and the careful study of its formation, and especially of its behaviour towards bromine, seems to indicate that

from the 1-methyl- Δ^3 -acid by intramolecular change during the long course of esterification and hydrolysis to which the mixed acids had been subjected:

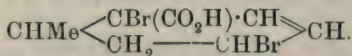


If this were correct, the *o*-menthadiene derived from the acid would contain conjugated double linkings, whereas the values actually found for the boiling point and refractive index of the menthadiene (see above) are so low that conjugation appears to be out of the question.

it is the $\Delta^{2:4}$ -dihydro-*o*-toluic acid (1-methyl- $\Delta^{2:4}$ -cyclohexadiene-2-carboxylic acid) of the formula:

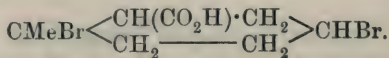


This acid absorbs bromine readily, with formation of a beautifully crystalline, unsaturated dibromo-acid, $\text{C}_8\text{H}_{10}\text{O}_2\text{Br}_2$, which melts at $147\text{--}148^\circ$, and does not yield a bromo-hydrocarbon when digested with sodium carbonate. The addition of only two atoms of bromine is, no doubt, due to the conjugated position of the double linkings, and the fact that boiling with sodium carbonate does not produce a bromo-hydrocarbon shows that the bromine atoms are not in the β -position in relation to the carboxyl group. If this behaviour be considered in connexion with the elimination of the hydroxyl group from the reduced 4-hydroxy-*o*-toluic acid, doubtless in the form of water, it is extremely probable that the above formula correctly represents the constitution of the dihydro-*o*-toluic acid of melting point 128° , and that the dibromo-additive product, $\text{C}_8\text{H}_{10}\text{O}_2\text{Br}_2$, is 2:5-dibromo-1-methyl- Δ^3 -cyclohexene-2-carboxylic acid:



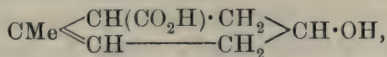
On two occasions, during the conversion of the mixture of acids obtained by the reduction of 4-hydroxy-*o*-toluic acid in the manner described on p. 748 into the corresponding bromo-acids by heating with hydrobromic acid, considerable quantities of a crystalline bromo-acid separated, which melts at $175\text{--}177^\circ$, and has the composition $\text{C}_8\text{H}_{12}\text{O}_2\text{Br}_2$.

In the previous paper on the reduction of 4-hydroxy-*o*-toluic acid (Trans., 1909, 95, 1875) it is shown that one of the products is a beautifully crystalline lactone, $\text{C}_8\text{H}_{10}\text{O}_2$ (m. p. 44°), which passes over when the product of reduction is distilled in a current of steam. This lactone reacts readily with hydrobromic acid, and yields a dibromo-acid, $\text{C}_8\text{H}_{12}\text{O}_2\text{Br}_2$ (m. p. $158\text{--}160^\circ$), which is probably *cis*-1:4-dibromo-1-methylcyclohexane-2-carboxylic acid:



One of the most characteristic properties of this dibromo-acid is the fact that its solution in sodium carbonate readily decomposes with separation of a heavy neutral oil containing bromine. The new dibromo-acid, melting at $175\text{--}177^\circ$, also exhibits this property, and there can be no doubt that the explanation of its formation is as follows. The product of the reduction of 4-hydroxy-*o*-toluic

acid doubtless contains the *cis*- and *trans*-modifications of 1-methyl- Δ^6 -cyclohexen-4-ol-2-carboxylic acid,

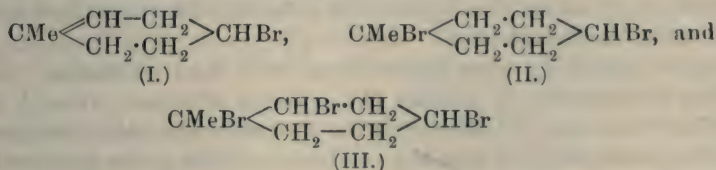


and of these the *cis*-modification is readily converted into the lactone and removed by distillation in a current of steam (*loc. cit.*, p. 1874).

The *trans*-modification remains in the residue from the steam distillation, and this, on treatment with hydrobromic acid, yields the dibromo-acid, melting at 175—177°, which is, therefore, in all probability, *trans*-1:4-dibromo-1-methylcyclohexane-2-carboxylic acid.

In possession of considerable quantities of this *trans*-dibromo-acid, its behaviour with sodium carbonate has been investigated, when the neutral oil produced was found to distil at 180°, and to have the composition $\text{C}_7\text{H}_{11}\text{Br}$. The formation of this substance is therefore due to the elimination of hydrogen bromide and carbon dioxide from the *trans*-dibromo-acid, and the substance $\text{C}_7\text{H}_{11}\text{Br}$ is probably 4-bromo-1-methyl- Δ^1 -cyclohexene (I).

This bromide combines readily with hydrogen bromide, with formation of a dibromide, $\text{C}_7\text{H}_{12}\text{Br}_2$ (b. p. 135°/40 mm.), and yields with bromine a crystalline tribromide, $\text{C}_7\text{H}_{11}\text{Br}_3$ (m. p. 58°), and these substances are probably 1:4-dibromo-1-methylcyclohexane (II) and 1:2:4-tribromo-1-methylcyclohexane (III):

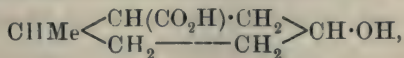


respectively.

EXPERIMENTAL.

*Preparation and Separation of 1-Methyl- Δ^3 -cyclohexene-2-carboxylic Acid, 1-Methyl- Δ^4 -cyclohexene-2-carboxylic Acid, Dihydro-*o*-toluic Acid, and *o*-Toluic Acid.*

The starting point in the preparation of these acids was the crude mixture of the *cis*- and *trans*-modifications of 1-methylcyclohexen-4-ol-2-carboxylic acid,



which was obtained in large quantities by the reduction of 4-hydroxy-*o*-toluic acid essentially according to the method already described (Trans., 1909, 95, 1876). This acid, in quantities of

50 grams, was mixed with twice its volume of fuming hydrobromic acid (saturated at 0°), and the mixture, after remaining for two days, gradually heated, first at about 60° for one hour, and then for two hours on the steam-bath, when a viscid, brown syrup separated. The product was mixed with water, extracted twice with ether, the ethereal solution washed, dried, evaporated, and the residue heated with 200 c.c. of 10 per cent. alcoholic sulphuric acid for several hours on the water-bath. Water was then added, the heavy bromo-ester extracted with ether, the ethereal solution washed, carefully dried, evaporated, and the residue boiled with three times its volume of diethylaniline for five hours. The dark brown product was mixed with excess of dilute hydrochloric acid, extracted with ether, the ethereal solution washed well with sodium carbonate, and then evaporated, and the crude, mixed, unsaturated esters distilled in a current of steam. The residue in the flask yielded a further quantity of unsaturated ester when the treatment with hydrobromic acid and diethylaniline was repeated. The unsaturated esters, volatile in steam, were extracted with ether, the ethereal solution washed with sodium carbonate,* evaporated, and the residue fractionated, when almost the whole quantity distilled at $135\text{--}150^{\circ}/100\text{ mm.}\dagger$

This ester was left in contact with a large excess of methyl-alcoholic potassium hydroxide in the cold until hydrolysis was complete; the product was then nearly neutralised with hydrochloric acid, saturated with carbon dioxide, and evaporated until free from methyl alcohol.

After acidifying with hydrochloric acid and extracting with ether, the acids were distilled in a current of steam, when it was noticed that towards the end of the operation the acid crystallised in the condenser, and that the residue, on cooling, also deposited a small quantity of a crystalline acid. This crystalline substance consists essentially of dihydro-*o*-toluic acid and *o*-toluic acid mixed with small quantities of *trans*-1-methyl- Δ^3 -cyclohexene-2-carboxylic acid (p. 758).

Since experiments on the separation of the mixture of 1-methyl- Δ^3 - and 1-methyl- Δ^4 -cyclohexene-2-carboxylic acids by conversion into a great variety of salts were unsuccessful, the process of fractional esterification had again to be resorted to, and the method employed was essentially the same as that already described in detail in the case of the separation of the Δ^5 - and Δ^6 -isomerides

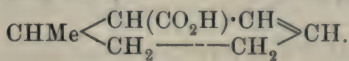
* The sodium carbonate extract yielded, on acidifying, a syrup which soon began to crystallise, owing to the separation of small quantities of dihydro-*o*-toluic and *o*-toluic acids (compare p. 758).

† If the ester is found to contain any considerable quantity of bromine, treatment with diethylaniline must be repeated.

(this vol., p. 733). That there is sufficient difference in the rates of esterification of the Δ^3 - and Δ^4 -acids, and in the rates of hydrolysis of their esters, is indicated by the following comparative experiments which were made with the esters after the process of separation had been carried out. These experiments were conducted exactly in the manner described in the case of the comparative hydrolysis of the esters of the Δ^5 - and Δ^6 -acids (this vol., p. 734), and showed that 80—82 per cent. of ethyl 1-methyl- Δ^4 -cyclohexene-2-carboxylate is hydrolysed under conditions which effect the hydrolysis of only 61—63 per cent. of the Δ^3 -ester.

During the long process of separation by fractional esterification and hydrolysis it was observed, especially during the first operations, that the sodium carbonate extracts from the esterification of the Δ^3 -acid deposited small quantities of an acid which became semi-solid in the ice-chest. When this was fractionally distilled in steam it yielded several grams of a mixture of *o*-toluic acid and dihydro-*o*-toluic acid (compare p. 758).

trans-1-Methyl- Δ^3 -cyclohexene-2-carboxylic Acid,



The esters of the *trans*- and *cis*-modifications of 1-methylcyclohexene-2-carboxylic acid constitute that portion of the unsaturated esters which is most difficult to hydrolyse, and, after the separation of the other more readily hydrolysed Δ^4 -ester had been systematically carried out in the way mentioned on p. 742, the *trans*- and *cis*-esters of the Δ^3 -acid were left with a considerable excess of methyl-alcoholic potassium hydroxide until the mixture was completely hydrolysed. The product was mixed with water, nearly neutralised with hydrochloric acid, saturated with carbon dioxide, and the methyl alcohol removed by distillation under diminished pressure.

The aqueous solution was then acidified, the acid extracted with ether, the ethereal solution carefully washed, dried, evaporated, and the residue distilled, when almost the whole quantity passed over at 162—163°/50 mm. On keeping in the ice-chest this acid soon commenced to crystallise, and, after several days, the semi-solid mass was placed in contact with porous porcelain, when the oil was rapidly absorbed and a colourless, crystalline mass remained, which, after rapidly washing with a little very light petroleum, was analysed:

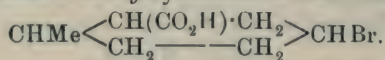
0.1092 gave 0.2783 CO_2 and 0.0861 H_2O . C=68.7; H=8.7.

$\text{C}_8\text{H}_{12}\text{O}_2$ requires C=68.6; H=8.6 per cent.

trans-1-Methyl- Δ^3 -cyclohexene-2-carboxylic acid melts at about 60—62°, and is so readily soluble in the usual organic solvents that no attempt was made to recrystallise it. It dissolves readily in sodium carbonate, and the solution instantly decolorises permanganate.

Ethyl trans-1-Methyl- Δ^3 -cyclohexene-2-carboxylate.—In preparing this ester the pure acid (12 grams) was mixed with alcohol (100 c.c.) and sulphuric acid (6 c.c.), and, after remaining for two days, the mixture was heated on the steam-bath for four hours. The product was mixed with water, extracted with ether, and the ethereal solution carefully washed with sodium carbonate, which removed 1.5 grams of unchanged acid, a fact which shows how difficult it is completely to esterify this *trans*-acid. The ethereal solution was then dried, evaporated, and the ester distilled, when the whole quantity passed over at 144—146°/100 mm. as a colourless oil, possessing a most penetrating and disagreeable odour.

trans-4-Bromo-1-methylcyclohexane-2-carboxylic Acid,



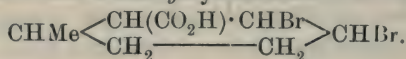
When *trans*-1-methyl- Δ^3 -cyclohexene-2-carboxylic acid is stirred with fuming hydrobromic acid (saturated at 0°), it liquefies, and the bromo-derivative separates on the surface of the acid as an oily layer, which soon crystallises. After remaining in contact with porous porcelain until quite dry, the bromo-acid was crystallised from formic acid, in which it is sparingly soluble in the cold, but readily so on warming.

The crystalline mass which separated softened at 90°, and was completely melted at 111°; it was obviously not homogeneous, but fractional crystallisation from formic acid ultimately yielded glistening plates, which melted sharply at 123—125°, and gave on analysis numbers agreeing with those required for the bromo-acid:

0.1551 gave 0.1317 AgBr. Br=36.1.

$\text{C}_8\text{H}_{13}\text{O}_2\text{Br}$ requires Br=36.2 per cent.

trans-3:4-Dibromo-1-methylcyclohexane-2-carboxylic Acid,



The solution of *trans*-1-methyl- Δ^3 -cyclohexene-2-carboxylic acid (0.34 gram) in a few drops of chloroform, cooled to -10°, readily absorbed 0.36 gram of bromine, whereas the amount required for the formation of the dibromo-acid is 0.38 gram. The product, poured on to a watch-glass and exposed to the air, soon crystallised,

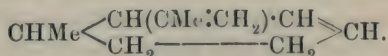
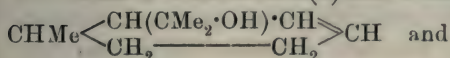
and, after draining on porous porcelain, the residue separated from light petroleum (b. p. 60—70°), in which it is sparingly soluble in the cold, in crusts:

0.1749 gave 0.2191 AgBr. Br=53.2.

$C_8H_{12}O_2Br_2$ requires Br=53.3 per cent.

This dibromo-acid melts and decomposes at about 125—126°; it dissolves in sodium carbonate, and, on warming, the solution clouds and a heavy oil separates, which has the odour of a bromo-hydrocarbon.

trans- Δ^3 - α -Menthenol(8) and trans- $\Delta^{3:8(9)}$ - α -Menthadiene,



The amount of ethyl *trans*-1-methyl- Δ^3 -cyclohexene-2-carboxylate available for conversion into the corresponding menthenol was, unfortunately, only 12 grams; this was mixed with an ethereal solution of magnesium methyl iodide containing 6 grams of magnesium, and, after remaining for two days, the product was decomposed by water and dilute hydrochloric acid, the ethereal solution washed, evaporated, and the residue distilled in a current of steam. The distillate was extracted with ether, the ethereal solution dried over anhydrous sodium sulphate, evaporated, and the residue distilled, when pure *trans- Δ^3 - α -menthenol(8)* passed over constantly at 110—111°/30 mm. as a rather limpid liquid which had a strong odour of menthol:

0.1151 gave 0.3284 CO_2 and 0.1238 CO_2 . C=77.7; H=11.9.

$C_{10}H_{18}O$ requires C=77.9; H=11.7 per cent.

trans- $\Delta^{3:8(9)}$ - α -Menthadiene was obtained from this menthenol by digesting with 6 per cent. oxalic acid for five hours, and then distilling in a current of steam. After extracting with ether and distilling twice alone and twice over sodium, it boiled constantly at 170°/760 mm., and had a rather faint odour of dipentene:

0.1257 gave 0.4069 CO_2 and 0.1373 H_2O . C=88.3; H=11.9.

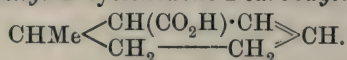
$C_{10}H_{16}$ requires C=88.2; H=11.8 per cent.

The physical constants, for the determination of which only a very small quantity of material was available, are approximately as follows:

$d_{20/20^\circ}$ 0.8477; n_D 1.4749; M 45.1, calc. $C_{10}H_{16}$ $[\alpha]_D^{25}$ 45.24,

and these values are appreciably lower than those observed in the case of the corresponding *cis*-modification (p. 753).

cis-1-Methyl- Δ^3 -cyclohexene-2-carboxylic Acid,



The porous plates which had been used in the purification of the *trans*-acid were broken up, extracted with ether in a Soxhlet apparatus, and the acid (62 grams) distilled and left in the ice-chest in contact with a crystal of the *trans*-acid for two months, when a further quantity of the *trans*-acid (4 grams) separated. This was collected and the process repeated, without, however, any more of the *trans*-acid crystallising out. The resulting oily acid was esterified by warming on the steam-bath with 8 per cent. alcoholic sulphuric acid for two hours, the ester extracted with ether, and shaken with sodium carbonate in the usual way, when it was noticed that the small quantity of acid obtained from the sodium carbonate extract, after distillation and leaving in the ice-chest for several days, deposited a small quantity of the *trans*-acid. As this behaviour indicated that the *cis*-acid esterified rather more rapidly than the *trans*-acid, the process of fractional esterification (compare p. 733) and hydrolysis was carried out five times, with the result that no further separation of *trans*-acid could be detected after the first two operations. The ester was then hydrolysed and the acid distilled, when it passed over constantly at 145—146°/20 mm.:

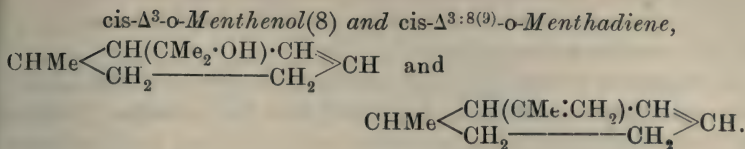
0.1754 gave 0.4395 CO₂ and 0.1334 H₂O. C=68.3; H=8.5.

C₈H₁₂O₂ requires C=68.6; H=8.6 per cent.

When prepared in this way *cis*-1-methyl- Δ^3 -cyclohexene-2-carboxylic acid probably still contains traces of the *trans*-modification, but the amount must be very small.

Ethyl cis-1-methyl- Δ^3 -cyclohexene-2-carboxylate was prepared by leaving the acid (20 grams) in contact with alcohol (150 c.c.) and sulphuric acid (5 c.c.) for two days and then heating on the steam-bath for one hour. After being isolated in the usual manner, it distilled constantly at 143—144°/100 mm., and had an odour which appeared to be even more pungent and unpleasant than that of the corresponding *trans*-ester. An experiment, made with the object of obtaining information as to the relative rates of hydrolysis of the *cis*- and *trans*-esters (compare p. 734), confirmed the observation that the former hydrolyses somewhat more rapidly than the latter, and indicated that the rates of hydrolysis were approximately in the ratio 18:16.5.

These numbers must, of course, be accepted as roughly approximate only.



In the preparation of the menthenol, ethyl *cis*-1-methyl- Δ^3 -cyclohexene-2-carboxylate (14 grams) was added to an ethereal solution of magnesium methyl iodide, containing 7 grams of magnesium, and, after two days, the product was decomposed by water and distilled in a current of steam. After extracting, drying over anhydrous sodium sulphate, and distilling, *cis*- Δ^3 - α -menthenol(8) was obtained as a rather limpid liquid boiling at 107—108°/30 mm., and having a pungent odour of terpineol and peppermint:

0.1293 gave 0.3697 CO₂ and 0.1386 H₂O. C = 77.9; H = 11.9.

C₁₀H₁₈O requires C = 77.9; H = 11.7 per cent.

cis- $\Delta^{3:8(9)}$ - α -Menthadiene was obtained from this menthenol by digesting with 6 per cent. oxalic acid for six hours, and then distilling in a current of steam. After extracting, carefully drying, and then distilling, first alone and then three times over sodium, the terpene boiled at 169—170°/762 mm., and had a pronounced odour somewhat resembling that of dipentene:

0.1371 gave 0.4427 CO₂ and 0.1486 H₂O. C = 88.1; H = 12.0.

C₁₀H₁₆ requires C = 88.2; H = 11.8 per cent.

The physical constants which had to be determined with small quantities of material gave rather high values, especially for the refractive index: $d_{20/20^\circ}$ 0.8507; n_D 1.4825; M 45.6; calc. for C₁₀H₁₆ $|\bar{r}|^2$ 45.24.

Oxidation of cis- and trans-1-Methyl- Δ^3 -cyclohexene-2-carboxylic Acids to β -Methyladipic Acid.

In this experiment the mixture of the *cis*- and *trans*-acids, obtained directly by the hydrolysis of the ester as explained on p. 749, was dissolved in a slight excess of dilute sodium carbonate, and a current of ozonised oxygen passed for several days until it escaped freely. The product was mixed with powdered ice and treated with 1 per cent. permanganate until the colour remained; the filtrate and washings of the manganese precipitate were acidified with hydrochloric acid, evaporated to dryness, extracted with ether in a Soxhlet apparatus, and, after the ether had been removed, the acid was heated at 180—200° until effervescence stopped. The dark brown residue was then converted into the ester by digesting with 10 per cent. alcoholic sulphuric acid, and fractionated, when

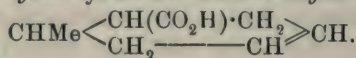
a considerable quantity passed over at 125—130°/10 mm., and there was a second smaller fraction at 187—190°/10 mm. which was not further investigated.

Examination showed that the fraction 125—130°/10 mm. is ethyl β -methyladipate. (Found, C=60·5; H=9·3. Calc., C=61·1; H=9·2 per cent.)

This ester was hydrolysed with methyl-alcoholic potassium hydroxide, the product mixed with water, evaporated until free from methyl alcohol, acidified, and repeatedly extracted with ether. The carefully dried ethereal solution deposited, on evaporation, a nearly colourless syrup, which soon crystallised, and, after remaining in contact with porous porcelain and then crystallising from dilute hydrochloric acid, a crystalline acid was obtained. (Found, C=52·1; H=7·5. Calc., C=52·5; H=7·5 per cent.)

This acid melted at 82—84°, and was proved to be β -methyladipic acid by admixture with a pure specimen of this acid when the mixture melted at 83—84°.

1-Methyl- Δ^4 -cyclohexene-2-carboxylic Acid,



This acid was prepared from the pure ester (p. 748) by leaving it in contact with excess of methyl-alcoholic potassium hydroxide for three days; water was then added, and traces of unhydrolysed ester removed by extraction with ether. The aqueous solution was nearly neutralised by hydrochloric acid, saturated with carbon dioxide, evaporated until free from methyl alcohol, and, after acidifying, the acid was extracted with pure ether, the ethereal solution dried thoroughly and evaporated, and the acid distilled under diminished pressure:

0·1755 gave 0·4380 CO₂ and 0·1316 H₂O. C=68·1; H=8·4.

C₈H₁₂O₂ requires C=68·6; H=8·6 per cent.

1-Methyl- Δ^4 -cyclohexene-2-carboxylic acid distils at 135°/12 mm., 143°/20 mm., or at 180—181°/100 mm., and is a viscid, colourless syrup which showed no signs of crystallising, even after remaining for several weeks in the ice-chest. *Ethyl 1-methyl- Δ^4 -cyclohexene-2-carboxylate* was prepared by leaving the acid (110 grams) in contact with alcohol (400 c.c.) and sulphuric acid (30 c.c.) for four days. The product was mixed with water, the ester extracted with ether, the ethereal solution washed well with sodium carbonate, dried, and distilled, when the whole quantity passed over at 140°/100 mm.:

0·1231 gave 0·3219 CO₂ and 0·1070 H₂O. C=71·3; H=9·7.

C₁₀H₁₆O₂ requires C=71·4; H=9·5 per cent.

5 - *Bromo-1-methylcyclohexane-2-carboxylic Acid*.—1-Methyl- Δ^4 -cyclohexene-2-carboxylic acid dissolves at once in fuming hydrobromic acid (saturated at 0°), and in a few seconds the solution clouds and an oil separates which gradually becomes semi-solid. In contact with porous porcelain the oily impurities were soon absorbed, and the residue separated from formic acid in colourless needles, which melted at 134° :

0.1557 gave 0.1318 AgBr. Br=36.0.

$C_8H_{13}O_2Br$ requires Br=36.2 per cent.

4:5-Dibromo-1-methylcyclohexane-2-carboxylic Acid.—The solution of 1-methyl- Δ^4 -cyclohexene-2-carboxylic acid (1.1 grams) in chloroform, cooled to -10° , rapidly decolorised bromine with elimination of a little hydrogen bromide, and the amount absorbed was about 1.2 grams, whereas theory requires 1.25 grams. The product was allowed to evaporate in a current of air, and the semi-solid residue was then rubbed with a little formic acid, transferred to porous porcelain, and crystallised from formic acid:

0.1513 gave 0.1874 AgBr. Br=52.8.

$C_8H_{12}O_2Br_2$ requires Br=53.3 per cent.

4:5-Dibromo-1-methylcyclohexane-2-carboxylic acid separates from formic acid as a granular mass, which softens at 140° and melts at about 150° . It dissolves in sodium carbonate, and the solution, when gently heated, suddenly clouds, and an oil separates which does not smell like a bromo-hydrocarbon, and is soluble in hot water; it is therefore probably a bromo-lactone.

Oxidation of 1-Methyl- Δ^4 -cyclohexene-2-carboxylic Acid to
 γ -Methylbutane- $\alpha\beta\delta$ -tricarboxylic Acid,
 $CO_2H \cdot CH_2 \cdot CH(CO_2H) \cdot CHMe \cdot CH_2 \cdot CO_2H$.

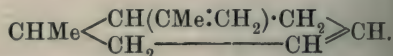
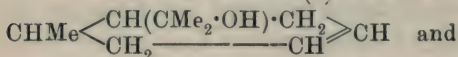
In this experiment the solution of the acid (10 grams) in a very slight excess of sodium carbonate was divided into two parts, and a stream of ozonised oxygen passed at the ordinary temperature for several days and until it escaped freely. The solution was then mixed with much powdered ice, treated with 1 per cent. permanganate until the colour remained, and, after the slight excess had been removed by sodium sulphite, the whole was heated on the steam-bath and filtered. The filtrate and washings from the manganese precipitate were evaporated to a small bulk, rendered just acid to Congo paper with hydrochloric acid, evaporated to dryness, mixed with sand, and extracted with ether in a Soxhlet apparatus. After distilling off the ether, the syrup was dissolved in water and oxidised on the steam-bath with excess of sodium dichromate and dilute sulphuric acid, and the product repeatedly extracted

mechanically with ether. The ethereal solution was thoroughly dried, evaporated, and the residue digested with 10 per cent. alcoholic sulphuric acid for two days; water was then added, the ester extracted with ether, the ethereal solution washed with sodium carbonate, dried, and evaporated. The ester distilled almost completely at 184—185°/20 mm. (Found, C=58·8; H=8·7. Calc., C=58·3; H=8·3 per cent.)

That this substance is the ester of γ -methylbutane- $\alpha\beta\delta$ -tricarboxylic acid, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is shown by its behaviour on hydrolysis. The ester was digested with 5 per cent. hydrochloric acid until it had completely dissolved, the clear solution evaporated to a small bulk, and left over solid potassium hydroxide in a vacuum desiccator, when the solution gradually deposited hard, warty masses, which, after recrystallisation from hydrochloric acid, melted at 153°. (Found, C=46·8; H=6·0. Calc., C=47·0; H=5·9 per cent.)

0·2332 neutralised 34·0 c.c. $N/10\text{-NaOH}$, whereas this amount of a tribasic acid, $\text{C}_8\text{H}_{12}\text{O}_6$, should neutralise 34·3 c.c. That this acid is γ -methylbutane- $\alpha\beta\delta$ -tricarboxylic acid is proved by the fact that, when it was mixed with a specimen of this acid which had been prepared synthetically (p. 762), the mixture melted at the same temperature as the constituents.

$\Delta^4\text{-o-Menthenol(8)}$ and $\Delta^{4:8(9)}\text{-o-Menthadiene}$,



The above menthenol was prepared in considerable quantity by adding ethyl 1-methyl- Δ^4 -cyclohexene-2-carboxylate, in quantities of 20 grams, to an ethereal solution of magnesium methyl iodide containing 9 grams of magnesium. After twenty-four hours the product was decomposed by water and dilute hydrochloric acid, the ethereal extract dried and evaporated, and the residue distilled under diminished pressure:

0·1500 gave 0·4290 CO_2 and 0·1592 H_2O . C=78·0; H=11·8.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires C=77·9; H=11·7 per cent.

$\Delta^4\text{-o-Menthenol(8)}$ is a rather viscid syrup, which distils at 110°/30 mm. and has a pungent odour of peppermint.

The Phenylurethane.—This derivative was prepared by leaving a mixture of the menthenol (1 gram) and phenylcarbimide (0·9 gram) in a sealed tube at the ordinary temperature for ten days. The crystalline product was mixed with a little light petroleum, transferred to porous porcelain, and the colourless residue crystal-

lised from dilute methyl alcohol, from which it separated in threads melting at 119—120°:

0.1069 gave 5.1 c.c. N_2 at 19° and 762 mm. $N=5.4$.

$C_{17}H_{23}O_2N$ requires $N=5.1$ per cent.

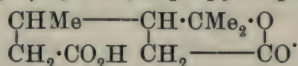
$\Delta^{4:8(9)}\text{-o-Menthadiene}$.—In preparing this terpene, $\Delta^4\text{-o-menthenol(8)}$, in quantities of 5 grams, was shaken mechanically with 500 c.c. of 5 per cent. sulphuric acid for ten days, and the product, after neutralisation, distilled in a current of steam. The distillate yielded, on extraction with ether, an oil, which, after distilling twice alone and then three times over sodium, boiled at 170—171°:

0.1490 gave 0.4798 CO_2 and 0.1602 H_2O . $C=87.8$; $H=11.9$.

$C_{10}H_{16}$ requires $C=88.2$; $H=11.8$ per cent.

This terpene has a pungent odour of peppermint and eucalyptus, and its solution in acetic anhydride gives, on the addition of a drop of sulphuric acid, a brown coloration, which becomes dark brownish-pink on keeping. When this terpene (0.85 gram), dissolved in chloroform (5 c.c.) and cooled to -10° , was titrated with bromine, it absorbed about 2.2 grams, but the end point was not sharp, and some hydrogen bromide was formed. The amount theoretically required for the formation of the additive compound, $C_{10}H_{16}Br_4$, is 2 grams.

Oxidation of $\Delta^4\text{-o-Menthenol(8)}$. Formation of the Lactone of β -Methyl- γ -hydroxyisopropyladipic Acid.



In studying this oxidation, the menthenol, in quantities of 1.5 grams, was shaken mechanically with water (100 c.c.), ice (100 grams), and a saturated solution of permanganate (4.2 grams) rendered alkaline by the addition of potassium hydroxide (2 grams) added in three quantities.

Traces of unchanged menthenol were removed by distillation in a current of steam, the whole filtered by the aid of the pump, and the filtrate and washings of the manganese precipitate rendered just acid to Congo paper and evaporated to dryness. On extracting the residue with ether in a Soxhlet apparatus, a brown syrup was obtained, which was dissolved in water, digested with purified animal charcoal, and the almost colourless solution evaporated to a small bulk and left over sulphuric acid for several days, when it partly crystallised. The mass was transferred to porous porcelain, and the nearly colourless residue crystallised from a little water, from which it separated in colourless prisms. This substance is the lactone of β -methyl- γ -hydroxyisopropyladipic acid, and was

obtained in this way only in a very small yield, but much larger quantities were ultimately isolated in the following manner. The porous plates, which had absorbed the syrupy impurity, were broken up, extracted in a Soxhlet apparatus, and the syrup boiled with 10 per cent. alcoholic sulphuric acid for ten hours. After adding water and extracting with ether, the ethereal solution was washed with sodium carbonate, dried, evaporated, and the residual ester fractionated, when almost the whole quantity passed over at 188—190°/20 mm.:

0.1362 gave 0.3128 CO₂ and 0.1089 H₂O. C=63.3; H=8.9.

C₁₂H₂₀O₄ requires C=63.2; H=8.8 per cent.

This ester of the lactone of β -methyl- γ -hydroxyisopropyladipic acid was hydrolysed by boiling with a large excess of 3 per cent. hydrochloric acid, the solution evaporated, and the nearly colourless syrup left over sulphuric acid, when it gradually crystallised and ultimately became nearly solid. After contact with porous porcelain, the substance was repeatedly crystallised from water:

0.1124 gave 0.2467 CO₂ and 0.0829 H₂O. C=59.9; H=8.2.

C₁₀H₁₆O₄ requires C=60.0; H=8.0 per cent.

The lactone of β -methyl- γ -hydroxyisopropyladipic acid melts at 113—114°, is rather sparingly soluble in cold water, but dissolves readily on warming, and the solution, on cooling, clouds, and then deposits glistening prisms. The lactone is rather sparingly soluble in ether, light petroleum, or benzene, and crystallises beautifully from ether as a crust of small, glistening prisms.

0.3122 Gram, dissolved in cold water, required for neutralisation 15.7 c.c. *N*/10-NaOH, whereas this quantity of a monobasic acid, C₁₀H₁₆O₄, should neutralise 15.6 c.c. In a second experiment, 0.2874 gram was boiled with 40 c.c. of *N*/10-sodium hydroxide, and the excess determined by titration with *N*/10-hydrochloric acid, when it was found that 28.4 c.c. had been neutralised, whereas this amount of a lactonic acid, C₁₉H₁₆O₄, becoming dibasic, requires 28.7 c.c.

The mother liquors of the above lactone contain another substance, which is probably the corresponding *cis*-modification, but all attempts to obtain it in a pure condition were unsuccessful.

$\Delta^2:4$ -Dihydro-*o*-toluic Acid (1-Methyl- $\Delta^2:4$ -cyclohexadiene-2-carboxylic Acid), CHMe < $\begin{matrix} \text{C}(\text{CO}_2\text{H})\text{:CH} \\ \text{CH}_2 \text{---} \text{CH} \end{matrix} \rangle \text{CH}$.

The material from which this acid was isolated was obtained in the largest quantity during the first purification of the crude unsaturated esters by the process described on p. 748, but other

small quantities were collected, especially during the purification of 1-methyl- Δ^3 -cyclohexenecarboxylic acid by fractional esterification and hydrolysis. The mixture of solid acids was collected and submitted to fractional distillation in steam, and thus separated into *trans*-1-methyl- Δ^3 -cyclohexene-2-carboxylic acid, which passed over first, and an acid, volatile with difficulty in steam, which crystallised from light petroleum in needles. (Found, C=70.5; H=6.1. Calc., C=70.6; H=5.9 per cent.)

This acid melted at 100—102°, and was *o*-toluic acid, since an admixture with a pure specimen of this acid melted at 101—102°.

The residue in the steam distillation flask contained a crystalline acid, which was collected, drained on porous porcelain, and crystallised from dilute acetic acid:

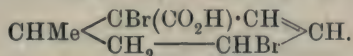
0.1256 gave 0.3188 CO₂ and 0.0821 H₂O. C=69.2; H=7.4.

0.1094 „ 0.2775 CO₂ „ 0.0725 H₂O. C=69.3; H=7.3.

C₈H₁₀O₂ requires C=69.5; H=7.2 per cent.

$\Delta^{2:4}$ -Dihydro-*o*-toluic acid melts at 128°, and is very sparingly soluble in cold water; it dissolves readily in warm chloroform, and separates, on cooling, as a beautiful, glistening, crystalline mass; it is also soluble in hot light petroleum (b. p. 80—90°), and crystallises, on cooling, as a crust of needles. The solution in sodium carbonate decolorises permanganate instantly. The constitution of this acid is discussed on p. 746.

2:5-Dibromo-1-methyl- Δ^3 -cyclohexene-2-carboxylic Acid,



When dihydro-*o*-toluic acid (0.303 gram), dissolved in chloroform and cooled to -10°, was titrated with a solution of bromine in chloroform, it absorbed 0.35 gram of bromine, which is exactly the theoretical quantity required for the formation of the dibromo-additive derivative. The chloroform was allowed to evaporate in a current of air, and the solid residue crystallised from formic acid, in which it is sparingly soluble in the cold, and from which it separates in pointed plates:

0.1283 gave 0.1526 CO₂ and 0.0404 H₂O. C=32.4; H=3.5.

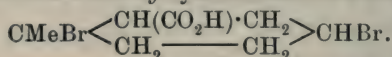
0.1393 „ 0.1479 AgBr. Br=53.3.

C₈H₁₀O₂Br₂ requires C=32.2; H=3.4; Br=53.7 per cent.

This dibromo-acid melts at 147—148°, and is readily soluble in alcohol, ether, benzene, or chloroform, but sparingly so in light petroleum. It crystallises from dilute alcohol in groups of jagged needles like pine leaves. When the finely divided acid is boiled

with much water it dissolves, apparently without much decomposition, since a crystalline acid separates on cooling, and the solution gives only an opalescence with silver nitrate; on the other hand, boiling with silver nitrate causes the rapid separation of silver bromide. The solution of the bromo-acid in sodium carbonate decolorises permanganate in a few seconds, but not immediately. When the solution in sodium carbonate is boiled, there is no separation of a bromo-hydrocarbon, and, on acidifying, a crystalline acid separates, which was not investigated.

trans-1:4-Dibromo-1-methylcyclohexane-2-carboxylic Acid,



As explained in the introduction (p. 746) this bromo-acid sometimes separated in considerable quantities when the product of the reduction of 4-hydroxy-*o*-toluic acid was treated with hydrobromic acid.

The dark-coloured crystalline mass was collected, left in contact with porous porcelain until quite dry, and then repeatedly recrystallised from benzene, from which it separated in glistening prisms, melting at 175—177° with vigorous decomposition:

0.1545 gave 0.1840 CO₂ and 0.0601 H₂O. C=32.4; H=4.4.

0.1890 „ 0.2332 AgBr. Br=52.5.

0.3411 „ 0.4231 AgBr. Br=52.8.

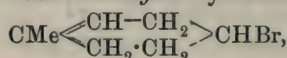
C₈H₁₂O₂Br₂ requires C=32.0; H=4.0; Br=53.3 per cent.

This bromo-acid is almost insoluble in light petroleum, and sparingly so in cold benzene, but dissolves readily in hot benzene and also in warm formic acid, from which latter it separates in jagged needles like pine leaves. A considerable quantity of this acid was ground to a paste with water and shaken with excess of sodium carbonate, when it dissolved, but the solution soon clouded, and a heavy oil separated. This was extracted with ether, the ethereal solution washed well, dried, evaporated, and the residue distilled, when almost the whole quantity passed over at 178—180° with hardly any decomposition:

0.4273 gave 0.4505 AgBr. Br=44.9.

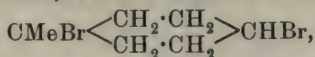
C₇H₁₁Br requires Br=45.6 per cent.

4-Bromo-1-methyl-Δ¹-cyclohexene,



is a heavy liquid with a pungent odour somewhat similar to that of isoamyl bromide. When this oil is shaken with fuming hydrobromic acid (saturated at 0°), it dissolves with considerable rise of

temperature, and, after keeping for two hours, the dark-coloured liquid was mixed with water and the heavy oil extracted with ether. The ethereal solution was washed well, dried, evaporated, and the residue distilled, when 1:4-dibromo-1-methylcyclohexane,



passed over as a colourless oil which has an odour resembling that of trimethylene bromide. It distils at about $135^\circ/40$ mm., but there is slight decomposition, and, owing to the elimination of traces of hydrogen bromide during distillation, the analytical results are somewhat too low:

0.1385 gave 0.1962 AgBr. Br = 60.4.

$\text{C}_7\text{H}_{12}\text{Br}_2$ requires Br = 62.5 per cent.

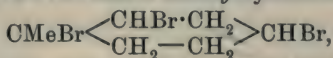
In investigating the action of bromine on 4-bromo-1-methylcyclohexene, the substance (1.149 grams) was dissolved in chloroform, cooled to -10° , and titrated with a standard solution of bromine in chloroform, when 0.92 gram of bromine was absorbed, whereas theory requires 0.90 gram for the formation of a dibromo-additive derivative.

The solution was allowed to evaporate, when a syrup remained, which gradually crystallised, and, after remaining in contact with porous porcelain until dry, the substance was washed on porous porcelain with a little low-boiling light petroleum, and then analysed:

0.1169 gave 0.1936 AgBr. Br = 70.5.

$\text{C}_7\text{H}_{11}\text{Br}_3$ requires Br = 71.7 per cent.

1:2:4-Tribromo-1-methylcyclohexane,



melts at $57-58^\circ$, and appears to distil in small quantities almost unchanged, since the distillate readily crystallises and very little hydrogen bromide is eliminated. It has a pungent odour like that of carbon tetrabromide, is very soluble in light petroleum, and crystallises from the highly concentrated solution in plates.

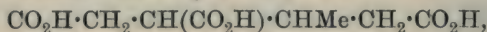
The author is indebted to Messrs. H. Hibbert and L. Benson for assistance in preparing and reducing the large amount of 4-hydroxy-o-toluic acid required for this research, and also to Miss B. Dobson for carrying out some of the analyses. The author is also grateful for the considerable grants from the Research Funds of the Royal Society and Chemical Society which have made this long and expensive investigation possible.

LXXXII.—*The Condensation of Ethyl Crotonate and Ethyl Methylacrylate with Ethyl Cyanoacetate and Ethyl Bromoacetate. Synthesis of γ -Methylbutane- $\alpha\beta\delta$ -tricarboxylic Acid and Pentane- $\alpha\beta\delta$ -tricarboxylic Acid.*

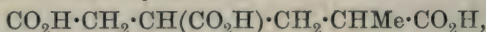
By EDWARD HOPE and WILLIAM HENRY PERKIN, jun.

DURING the course of the investigations described in the preceding communications certain acids were obtained which had not previously been prepared, and which it was necessary to identify.

Since it seemed probable that one of these acids might be either γ -methylbutane- $\alpha\beta\delta$ -tricarboxylic acid,

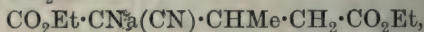
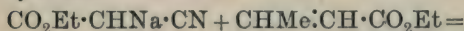


or pentane- $\alpha\beta\delta$ -tricarboxylic acid,

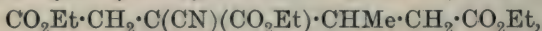


we decided to attempt the synthesis of these acids in order to allow of a direct comparison. The method adopted in the case of the synthesis of the γ -methyl acid was the following one:

Ethyl crotonate was digested with the sodium derivative of ethyl cyanoacetate,



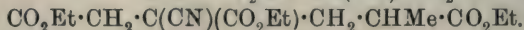
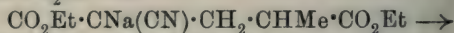
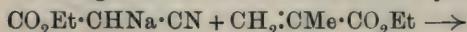
and the product of condensation treated with ethyl bromoacetate, when ethyl β -cyano- γ -methylbutane- $\alpha\beta\delta$ -tricarboxylate,



was obtained, and this, on hydrolysis and elimination of carbon dioxide, yielded γ -methylbutane- $\alpha\beta\delta$ -tricarboxylic acid, which melts at 153—154°. Careful comparison showed that this acid is identical with the acid which was obtained (p. 743) from 1-methyl- Δ^4 -cyclohexene-2-carboxylic acid by oxidation:

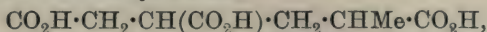


Subsequently ethyl β -cyanopentane- $\alpha\beta\delta$ -tricarboxylate was obtained in a similar manner by condensing ethyl methylacrylate with the sodium derivative of ethyl cyanoacetate, and treating the resulting sodium derivative with ethyl bromoacetate:



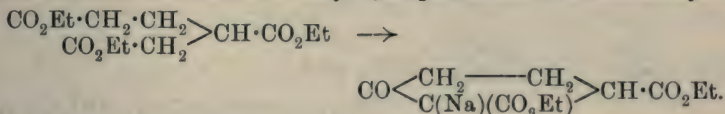
This cyano-ester is readily hydrolysed by boiling with dilute

hydrochloric acid, with elimination of carbon dioxide, and formation of pentane- $\alpha\beta\delta$ -tricarboxylic acid,

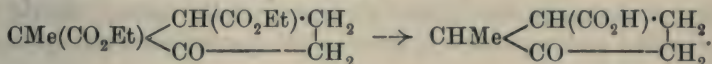


which crystallises well, and melts at 158° .

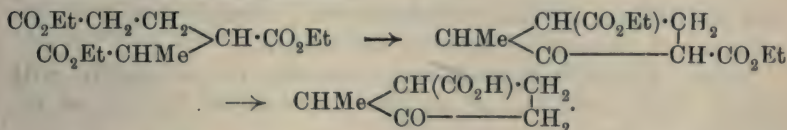
Our other object in carrying out these experiments was to attempt to supplement the work of Haworth and Perkin (Trans., 1908, **93**, 573) by preparing new *cyclopentanone*carboxylic acids which might then be employed in the synthesis of new terpineols and terpenes of the *cyclopentane* series. During the course of their experiments (compare Kay and Perkin, Trans., 1906, **89**, 1641) the action of sodium on ethylbutane- $\alpha\beta\delta$ -tricarboxylate was investigated, and it was shown that the reaction leads to the formation of the sodium derivative of ethyl *cyclopentanone*-2:3-dicarboxylate:



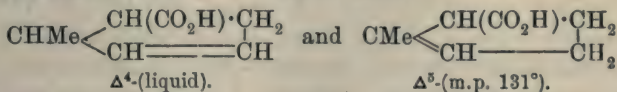
This sodium derivative reacts readily with methyl iodide with the production of ethyl 1-methyl*cyclopentan*-5-one-1:2-dicarboxylate, which, on hydrolysis with dilute hydrochloric acid, yields 1-methyl*cyclopentan*-5-one-2-carboxylic acid*:



The same acid was also obtained from the product of the action of sodium on ethyl pentane- $\beta\gamma\epsilon$ -tricarboxylate by hydrolysis and elimination of carbon dioxide:



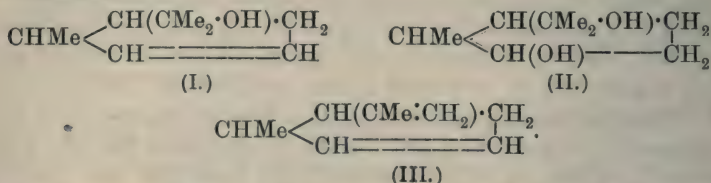
This ketonic acid is readily reduced to 1-methyl*cyclopenten*-5-ol-2-carboxylic acid, and the corresponding bromo-acid yields, on elimination of hydrogen bromide, a mixture of 1-methyl- Δ^4 - and 1-methyl- Δ^5 -*cyclopentene*-2-carboxylic acids:



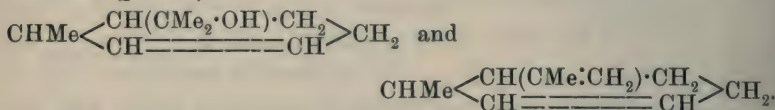
The ester of the Δ^4 -acid reacts readily with magnesium methyl

* These substances were originally named ethyl 2-methyl*cyclopentanone*-2:3-dicarboxylate and 2-methyl*cyclopentanone*-3-carboxylic acid, but, in view of the fact that the position assigned to the methyl group in the case of the methyl*cyclohexanone*s and their derivatives is always the position 1, it is desirable that the same practice should be observed in the *cyclopentanone* series.

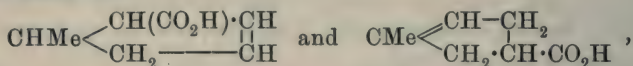
iodide, with the formation of 1-methyl-2-hydroxyisopropyl- Δ^4 -cyclopentene (I), from which, by the action (a) of dilute sulphuric acid, and (b) of dehydrating agents, 1-methyl-2-hydroxyisopropylcyclopentan-5-ol (II) and 1-methyl-2-isopropenyl- Δ^4 -cyclopentene (III) are obtained:



The substances I and III are of special interest when they are considered in connexion with Δ^5 -*o*-menthenol(8) and $\Delta^{5:8(9)}$ -*o*-menthadiene (p. 729):

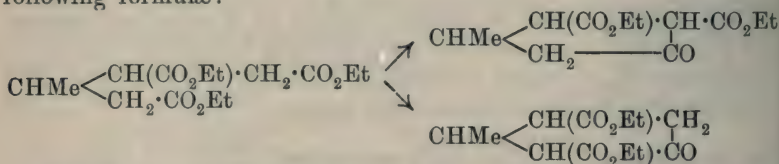


to which they are obviously closely related. The curious properties of the five-membered cyclic compounds just mentioned and their remarkable tendency to polymerise (compare *Trans.*, 1908, **93**, 579) made it desirable that other members of the group should be synthesised and examined in detail. This necessitated the synthesis of such acids as:

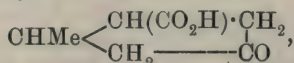


and we describe in this communication preliminary steps in the synthesis of unsaturated acids of this nature.

Ethyl γ -methylbutane- $\alpha\beta\delta$ -tricarboxylate reacts readily with sodium with formation of an ester represented by one of the following formulæ:

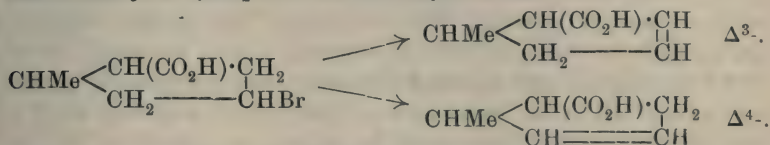


For the purposes of this investigation it is immaterial which formula represents this ester, because in both cases hydrolysis and elimination of carbon dioxide leads to the same 1-methylcyclopentan-4-one-2-carboxylic acid,

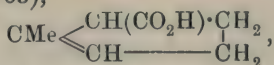


a crystalline substance which melts at 49–50°, and of which a

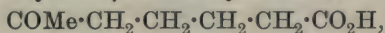
number of derivatives are described. This acid is readily reduced to 1-methylcyclopentan-4-ol-2-carboxylic acid, and when the ester of the corresponding bromo-acid was treated with diethylaniline and hydrolysed we were surprised to find that, whilst the main product of the reaction was doubtless a mixture of 1-methyl- Δ^3 - and 1-methyl- Δ^4 -cyclopentene-2-carboxylic acids:



small quantities of 1-methyl- Δ^5 -cyclopentene-2-carboxylic acid (m. p. 131° : see p. 763),



were also produced. Since the constitution of this acid is proved by the fact that it yields γ -acetobutyric acid,

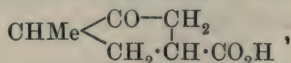


on oxidation (Trans., 1908, **93**, 588), it follows that a remarkable intramolecular change, due to the wandering of the double linking in the direction of the methyl group, must have taken place, probably during the elimination of hydrogen bromide from ethyl 4-bromo-1-methylcyclopentane-2-carboxylate and subsequent hydrolysis.

A series of experiments on the action of sodium on ethyl pentane- $\alpha\beta\delta$ -tricarboxylate has also been commenced, and in this case again, decomposition proceeds readily and a good yield of ethyl 1-methylcyclopentan-2-one-3:4-dicarboxylate:



is produced. This ester is readily hydrolysed by boiling with dilute hydrochloric acid with elimination of carbon dioxide and formation of 1-methylcyclopentan-2-one-4-carboxylic acid,



which is a syrup, and distils at $162\text{--}165^\circ/12$ mm. Owing to the difficulty of obtaining this keto-acid in quantity, no attempt has yet been made to reduce it, and the investigation of the nature of the unsaturated acids which would result from the direct or indirect elimination of water must be postponed until a better method for the preparation of the hydroxy-acid has been discovered.

EXPERIMENTAL.

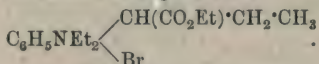
Ethyl β-Cyano-γ-methylbutane-αβδ-tricarboxylate,
 $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{CN})(\text{CO}_2\text{Et})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}.$

In the first experiments on the synthesis of this ester, sodium (11.6 grams) dissolved in alcohol (150 c.c.) was mixed with ethyl cyanoacetate (57 grams); ethyl crotonate* (58 grams) was then added, and the whole heated on the steam-bath for thirty hours. When the product was digested with ethyl bromoacetate (95 grams) and worked up in the usual manner (see below), it gave a yield of ethyl β-cyano-γ-methylbutane-αβδ-tricarboxylate, which at the best was only 55—60 per cent. of that theoretically possible, and often much less than this.

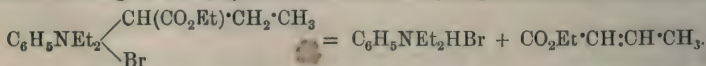
As large quantities of this ester were required, this loss was serious, and comparative experiments were therefore made in order to determine the best conditions for the formation of this ester, and ultimately the following process was adopted. Sodium (17.5 grams) is melted under toluene, and shaken so as to bring it into as fine a state of division as possible; the toluene is poured off, replaced by dry benzene (200 c.c.), ethyl cyanoacetate (85 grams) is then added, and the whole allowed to remain until the formation of the sodium derivative is complete. The cold product is mixed with ethyl crotonate (87 grams) and digested on the steam-bath for twenty-four hours; it is then well cooled, and ethyl bromoacetate (150 grams) added in small quantities; finally, the whole is heated

* Much of the ethyl crotonate required for our first experiments was prepared from ethyl α-bromobutyrate by digesting with diethylaniline in an apparatus which allowed of the volatile products, which might be formed, being collected and investigated, when it was noticed that large quantities of ethyl bromide distilled over during the operation and the yield of ethyl crotonate was only 35 per cent. of that theoretically possible. A possible explanation of this curious reaction is this:

Diethylaniline may react to some extent directly as an agent for the elimination of hydrogen bromide, but it doubtless combines to a great extent with the ethyl α-bromobutyrate to form the additive compound (A)



This, at the temperature of the boiling diethylaniline, then loses ethyl bromide with formation of the compound $\text{C}_6\text{H}_5\text{NEt}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CH}_3$, and it is doubtless to the presence of large quantities of this substance that the low yield of ethyl crotonate is due. It is also possible that some ethyl crotonate may be derived from the additive compound (A) by the elimination of hydrogen bromide, thus:



A similar explanation applies to the cases investigated by Le Sueur and Haas (Trans, 1910, 97, 175; compare *ibid.*, 1909, 95, 273).

for fifteen minutes on the steam-bath to complete the reaction. After adding ether and water, the pale yellow oily layer is separated, washed several times with water, dried and evaporated, and the residue distilled, when ethyl β -cyano- γ -methylbutane- $\alpha\beta\delta$ -tricarboxylate passes over at $204\text{--}214^\circ/15$ mm., the yield being 90 per cent. of that theoretically possible. On redistillation, almost the whole quantity boiled at $205\text{--}208^\circ/13$ mm.:

0.1451 gave 0.3056 CO_2 and 0.0955 H_2O . $\text{C}=57.4$; $\text{H}=7.3$.

$\text{C}_{15}\text{H}_{23}\text{O}_6\text{N}$ requires 57.5; $\text{H}=7.3$ per cent.

γ -Methylbutane- $\alpha\beta\delta$ -tricarboxylic Acid,
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

In preparing this acid, ethyl β -cyano- γ -methylbutane- $\alpha\beta\delta$ -tricarboxylate, in quantities of 40 grams, was boiled with 40 per cent. sulphuric acid (170 c.c.) for about eighteen hours and until the oil had entirely disappeared. The yellowish-brown solution was saturated with ammonium sulphate, extracted three times with ether, the ethereal solution dried, evaporated, and the crude acid (110 grams) converted into the ester by leaving it with alcohol (450 c.c.) and concentrated sulphuric acid (110 c.c.) for three days at the ordinary temperature. The product was mixed with water, extracted with ether, the ethereal solution thoroughly washed with sodium carbonate, dried, evaporated, and the residue distilled, when the *ethyl γ -methylbutane- $\alpha\beta\delta$ -tricarboxylate* passed over constantly at $180\text{--}183^\circ/20$ mm.:

0.1652 gave 0.3509 CO_2 and 0.1197 H_2O . $\text{C}=58.0$; $\text{H}=8.0$.

$\text{C}_{14}\text{H}_{24}\text{O}_6$ requires $\text{C}=58.3$; $\text{H}=8.3$ per cent.

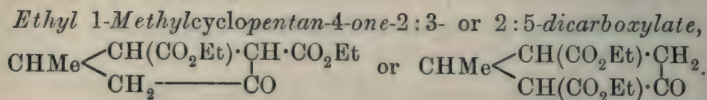
The amount of ester obtained directly was only 40—50 per cent. of that theoretically possible, and all attempts to improve the yield by digesting the acid with alcohol and sulphuric acid under different conditions were unsuccessful, and the product, in several cases, was not so pure. The sodium carbonate extract contains, however, partly esterified acid, which, when treated with alcohol and sulphuric acid under the same conditions as before, yields further quantities of ester.

In order to obtain the pure acid the ester is digested with an excess of methyl-alcoholic potassium hydroxide, and the crystalline potassium salt which separates collected, dried, dissolved in water, decomposed by hydrochloric acid, and the acid extracted several times with ether. After drying, the ethereal solution deposits on evaporation a colourless, crystalline acid, which is purified by crystallisation from hydrochloric acid, from which it gradually separates in nodular masses:

0.1223 gave 0.2096 CO_2 and 0.0683 H_2O . $\text{C}=46.7$; $\text{H}=6.2$.

$\text{C}_8\text{H}_{12}\text{O}_6$ requires $\text{C}=47.1$; $\text{H}=5.9$ per cent.

On titration with $N/10\text{-NaOH}$, 0.5231 neutralised 0.2984, whereas this amount of a tribasic acid, $\text{C}_8\text{H}_{12}\text{O}_6$, should neutralise 0.3082 NaOH . γ -Methylbutane- $\alpha\beta\delta$ -tricarboxylic acid melts at $153\text{--}154^\circ$, and is very soluble in water, but rather sparingly so in hydrochloric acid.



The ester possessing one of the above constitutional formulæ (compare p. 764) is produced by the action of sodium on ethyl γ -methylbutane- $\alpha\beta\delta$ -tricarboxylate. Sodium (11.5 grams) is granulated by melting under boiling toluene and shaking, the toluene is decanted and replaced by a solution of ethyl methylbutanetricarboxylate (72 grams) in benzene (80 c.c.), and the whole heated on the steam-bath for a few minutes. As soon as the vigorous reaction starts, the flask is temporarily removed from the steam-bath, but replaced again when the reaction subsides, and heated for three hours. The cold product is mixed with ether, the sodium derivative decomposed by dilute hydrochloric acid, the benzene-ether layer separated, washed well with water, the ether and benzene distilled off, and the residue fractionated, when almost the whole quantity distils at $168\text{--}171^\circ/18\text{ mm.}$, the yield being 70 per cent. of that theoretically possible:

0.1648 gave 0.3576 CO_2 and 0.1173 H_2O . $\text{C}=59.2$; $\text{H}=7.7$.

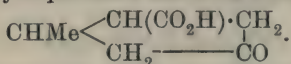
$\text{C}_{12}\text{H}_{18}\text{O}_5$ requires $\text{C}=59.5$; $\text{H}=7.4$ per cent.

Ethyl 1-methylcyclopentan-4-one-dicarboxylate is an almost colourless oil, which gives, in alcoholic solution, a violet coloration with ferric chloride. The semicarbazone was prepared by making an emulsion of the ester with hot water, adding semicarbazide hydrochloride and sodium acetate, and then heating to boiling for a few minutes. The oil which separated on cooling gradually crystallised, and, after collecting and recrystallising from ethyl acetate, the semicarbazone of the keto-ester was obtained in glistening crystals, which melted at $114\text{--}116^\circ$ without decomposition:

0.1904 gave 23.6 c.c. N_2 at 17° and 760 mm. $\text{N}=14.4$.

$\text{C}_{13}\text{H}_{21}\text{O}_5\text{N}_3$ requires $\text{N}=14.0$ per cent.

1-Methylcyclopentan-4-one-2-carboxylic Acid.



This acid is obtained when ethyl 1-methylcyclopentan-4-onedicarboxylate (20 grams) is boiled with 6 per cent. hydrochloric acid (200 c.c.), hydrolysis and elimination of carbon dioxide taking place simultaneously.

The solution is saturated with ammonium sulphate, extracted three times with ether, the ethereal solution dried, evaporated, and the ketonic acid distilled, when it passes over constantly at 175—177°/15 mm. as a syrup, which gradually crystallises and becomes semi-solid.

After contact with porous porcelain and rapidly washing with a little ether, the acid melted at 49—50°, and was so readily soluble that no attempt was made to recrystallise it. It is curious that, owing apparently to the presence of small quantities of some neutral impurity, we have been unable to obtain good results either from the analysis or titration of this acid:

0.1570 gave 0.3338 CO₂ and 0.0984 H₂O. C=58.0; H=6.9.

C₇H₁₀O₃ requires C=59.1; H=7.1 per cent.

On titration with *N*/10-NaOH, 0.2564 neutralised 0.0643, whereas this amount of a monobasic acid, C₇H₁₀O₃, should neutralise 0.0723 NaOH.

The *oxime* was prepared by mixing the acid (1.5 grams) with a concentrated solution of hydroxylamine hydrochloride (1.5 grams), and then adding potassium hydroxide (3 grams). After twenty-four hours the solution was acidified, extracted with ether, and the ethereal solution evaporated, when a syrup remained which soon solidified. For analysis the oxime was recrystallised from ether and then melted at 135—136°:

0.1085 gave 8.4 c.c. N₂ at 17° and 760 mm. N=8.9.

C₇H₁₁O₃N requires N=8.9 per cent.

The *semicarbazone* was prepared by boiling the solution of the acid with semicarbazide hydrochloride and sodium acetate, and separated, on cooling, as a white powder, which was recrystallised from water. It melts and decomposes at 215—217°:

0.1346 gave 24.4 c.c. N₂ at 18° and 760 mm. N=20.9.

C₈H₁₃O₃N₃ requires N=21.2 per cent.

Ethyl 1-Methylcyclopentan-4-one-2-carboxylate.—This ester was prepared by digesting the acid with alcoholic sulphuric acid (10 per cent. by volume) for five hours on the steam-bath. After pouring into water and extracting with ether in the usual way, an oil

was obtained which distilled constantly at $128^{\circ}/19$ mm. and consisted of the pure ester:

0.1283 gave 0.2990 CO_2 and 0.0974 H_2O . $\text{C}=63.5$; $\text{H}=8.4$.

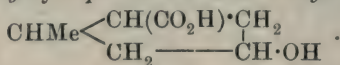
$\text{C}_9\text{H}_{14}\text{O}_3$ requires $\text{C}=63.5$; $\text{H}=8.2$ per cent.

The *semicarbazone* of the ester was prepared by shaking the ester with hot water until an emulsion formed, and then adding a hot solution of semicarbazide hydrochloride and sodium acetate. The product was at first oily, but solidified on keeping, and, after crystallisation from ether, melted at 124 — 126° without decomposition:

0.1202 gave 20.4 c.c. N_2 at 19° and 734 mm. $\text{N}=18.7$.

$\text{C}_{10}\text{H}_{17}\text{O}_3\text{N}_3$ requires $\text{N}=18.5$ per cent.

1-Methylcyclopentan-4-ol-2-carboxylic Acid,



In preparing this hydroxy-acid, 1-methylcyclopentan-4-one-2-carboxylic acid (25 grams) was dissolved in sodium carbonate and reduced, in a bottle fitted with a mechanical stirrer, with 1.5 kilos. of 3 per cent. sodium amalgam, which was added in several quantities.

During the operation, which lasted about five hours, a rapid stream of carbon dioxide was passed, and the temperature kept at 80° by passing steam into the water which surrounded the bottle. The product was acidified, saturated with ammonium sulphate, extracted several times with ether, the ethereal solution dried, and evaporated. When a small amount of the residue was fractionated, the hydroxy-acid distilled at 183 — $185^{\circ}/16$ mm. with considerable decomposition as a very viscid syrup, which did not crystallise. An attempt was made to eliminate water from this acid, and thus obtain the corresponding unsaturated acid, by digesting the acid with acetyl chloride and then distilling. No unsaturated acid was, however, formed, and the product distilled almost entirely at 218 — $223^{\circ}/16$ mm. as a viscid syrup which appeared to be the anhydride of 4-acetoxy-1-methylcyclopentane-2-carboxylic acid.

Ethyl 1-Methylcyclopentan-4-ol-2-carboxylate.—This ester was prepared by digesting the crude hydroxy-acid for several hours with 10 per cent. (by volume) alcoholic sulphuric acid; water was then added, the hydroxy-ester extracted with ether, the ethereal solution washed thoroughly with water and sodium carbonate, dried, and evaporated. The hydroxy-ester distilled constantly at 127 — $128^{\circ}/13$ mm. as a colourless oil with a faint, rather pleasant,

odour, but a small fraction was also obtained, boiling at 212—218°/12 mm., which was not further examined:

0.1211 gave 0.2778 CO₂ and 0.1030 H₂O. C=62.5; H=9.4.

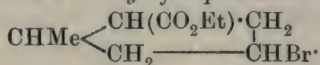
C₉H₁₆O₃ requires C=62.8; H=9.3 per cent.

When this ester was digested with acetyl chloride for several hours and the product distilled, a colourless oil, possessing an agreeable odour, passed over at 183°/100 mm., which analysis showed was *ethyl 4-acetoxy-1-methylcyclopentane-2-carboxylate*:

0.1202 gave 0.2703 CO₂ and 0.0908 H₂O. C=61.3; H=8.4.

C₁₁H₁₈O₄ requires C=61.7; H=8.4 per cent.

Ethyl 4-Bromo-1-methylcyclopentane-2-carboxylate,

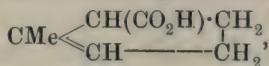


This bromo-ester was prepared by mixing 1-methylcyclopentan-4-ol-2-carboxylic acid with three times its volume of fuming hydrobromic acid (saturated at 0°), and, after remaining for half an hour, the whole was gradually heated on the steam-bath until the fumes of hydrogen bromide had practically ceased. The bromo-acid, which separated as a dark blue oil, was extracted with ether, the ethereal solution dried, evaporated, and the crude product immediately esterified by leaving it in contact with alcoholic sulphuric acid (10 per cent. by volume) for twenty-four hours. After pouring into water, extracting with ether, washing with sodium carbonate, drying, and evaporating, ethyl 4-bromo-1-methylcyclopentane-2-carboxylate was obtained as a colourless oil with a pungent odour, which distilled at 123—125°/20 mm.:

0.1011 gave 0.0795 AgBr. Br=33.5.

C₉H₁₅O₂Br requires Br=34.0 per cent.

The sodium carbonate extract from the purification of this bromo-ester yielded, on acidifying and extracting with ether, a small quantity of a crystalline, unsaturated acid, which was free from bromine, and crystallised from light petroleum in diamond-shaped plates. This acid melted at 131—132°, and proved to be identical with the 1-methyl-Δ⁵-cyclopentene-2-carboxylic acid,



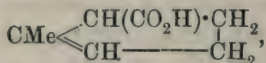
obtained by Haworth and Perkin (m. p. 130—131°) (Trans., 1908, 93, 586), since comparative experiments showed that the acids crystallised in exactly the same way, and that when mixed the mixture melted at the same temperature as the constituents. The remarkable formation of this acid from 1-methylcyclopentan-4-ol-2-carboxylic acid is discussed on p. 765.

Elimination of Hydrogen Bromide from Ethyl 4-Bromo-1-methylcyclopentane-2-carboxylate.—When this bromo-ester is gently boiled with twice its weight of diethylaniline for four hours, hydrogen bromide is readily and completely eliminated, and with very little darkening of the liquid. The product was mixed with ether and excess of dilute hydrochloric acid, the ethereal solution several times washed with dilute hydrochloric acid, dried, evaporated, and the unsaturated ester distilled, when almost the whole quantity passed over at 114—117°/100 mm. as a colourless liquid possessing a penetrating and very unpleasant odour:

0.1322 gave 0.3377 CO₂ and 0.1070 H₂O. C=69.7; H=9.0.

C₉H₁₄O₂ requires C=70.1; H=9.1 per cent.

Careful investigation indicates that this oil is a mixture of small quantities of the ester of 1-methyl- Δ^5 -cyclopentene-2-carboxylic acid,



together with the esters of the Δ^3 - and Δ^4 -isomerides, in which the two latter appear largely to predominate. The oil was digested for fifteen minutes with excess of methyl-alcoholic potassium hydroxide, water was then added, and the methyl alcohol removed by evaporation. The aqueous solution was acidified with hydrochloric acid, extracted with ether, the ethereal solution dried and distilled, when almost the whole quantity passed over at 157—160°/100 mm. as a colourless oil which showed no signs of crystallising:

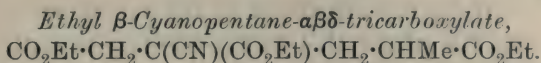
0.1420 gave 0.3452 CO₂ and 0.1040 H₂O. C=66.3; H=8.1.

C₇H₁₀O₂ requires C=66.7; H=7.9 per cent.

This acid decolorised permanganate instantly in the cold, and its solution in chloroform rapidly absorbed bromine and yielded a syrupy bromo-acid, which ultimately solidified, and, after recrystallisation from light petroleum, melted at 97—104°, but its appearance suggested that it was not a single substance. That the acid is a mixture was proved by the following experiment: The whole quantity was mixed with five times its volume of cold alcoholic sulphuric acid (10 per cent. by volume), and, after twenty-four hours, water was added, the product extracted with ether, and the ethereal solution well washed with sodium carbonate. When the sodium carbonate extract was acidified and extracted with ether, it yielded a crystalline acid, which, after contact with porous porcelain and recrystallisation from light petroleum, melted at 129—130°, and was shown by direct comparison to be 1-methyl- Δ^5 -cyclopentene-2-carboxylic acid (see above).

The ester which was produced in this experiment consisted,

apparently, of a mixture of ethyl 1-methyl- Δ^3 - and ethyl 1-methyl- Δ^4 -cyclopentene-2-carboxylate.



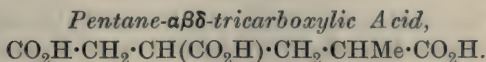
This ester is produced by the condensation of ethyl α -methylacrylate, $\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, with the sodium derivative of ethyl cyanoacetate, and subsequent treatment with ethyl bromoacetate.

In preparing the ethyl methylacrylate required for these experiments, the action of diethylaniline on ethyl α -bromoisobutyrate was first investigated, and it was found that in this case also, as in the case of ethyl α -bromobutyrate (footnote, p. 766), much ethyl bromide was produced, and the yield of unsaturated ester was only 15 per cent. of the theoretical amount (compare Howles, Thorpe, and Udall, *Trans.*, 1900, **77**, 947). Comparative experiments with quinoline showed that, although still unsatisfactory, the yield of unsaturated ester was much better, and accordingly the following process was ultimately adopted.

Ethyl α -bromoisobutyrate (150 grams) is mixed with quinoline (200 grams), and the whole heated on the sand-bath in a flask connected with a condenser until decomposition sets in. When once it starts, the reaction is a violent one, and all the ethyl methylacrylate which is produced distils into the receiver during the course of about ten minutes. If the residue in the flask is further heated, it is converted into a tar, from which quinoline cannot be recovered. The yield of ethyl methylacrylate obtained in this process is about 30—35 per cent. of that theoretically possible. The condensation of this unsaturated ester with the sodium derivative of ethyl cyanoacetate and subsequent treatment with ethyl bromoacetate was carried out in benzene solution under the conditions already described in the case of the condensation with ethyl crotonate (p. 766), and the *ethyl β -cyanopentane- $\alpha\beta\delta$ -tricarboxylate*, obtained in a good yield, is a viscid, straw-coloured oil, which distils at 204—207°/13 mm. without decomposition:

0.1409 gave 0.2947 CO_2 and 0.0932 H_2O . $\text{C}=57.0$; $\text{H}=7.3$.

$\text{C}_{15}\text{H}_{23}\text{O}_6\text{N}$ requires $\text{C}=57.5$; $\text{H}=7.3$ per cent.



This acid was obtained from ethyl β -cyanopentane- $\alpha\beta\delta$ -tricarboxylate by hydrolysis with 40 per cent. sulphuric acid, and was purified by conversion into the ester, the process being exactly similar to that described in the case of the γ -methyl acid (p. 767).

Ethyl pentane- $\alpha\beta\delta$ -tricarboxylate is a colourless oil, which distils at 170—174°/13 mm.:

0.1410 gave 0.2998 CO_2 and 0.1096 H_2O . $\text{C}=58.0$; $\text{H}=8.6$.

$\text{C}_{14}\text{H}_{24}\text{O}_6$ requires $\text{C}=58.3$; $\text{H}=8.3$ per cent.

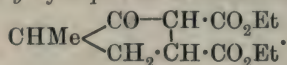
On treating this ester with a boiling solution of methyl-alcoholic potassium hydroxide, a white potassium salt rapidly separated, and was collected, freed from methyl alcohol, and decomposed in aqueous solution with hydrochloric acid. The acid obtained from the solution by extraction with ether crystallised much more readily than the corresponding γ -methyl acid, and was purified by recrystallisation from hydrochloric acid, from which it separated in crusts:

0.1500 gave 0.2591 CO_2 and 0.0850 H_2O . $\text{C}=47.1$; $\text{H}=6.3$.

$\text{C}_8\text{H}_{12}\text{O}_6$ requires $\text{C}=47.1$; $\text{H}=5.9$ per cent.

Pentane- $\alpha\beta\delta$ -tricarboxylic acid melts at 158°, and is readily soluble in water, acetone, or ethyl acetate, but sparingly so in benzene, chloroform, or light petroleum.

Ethyl 1-Methylcyclopentan-2-one-3:4-dicarboxylate,



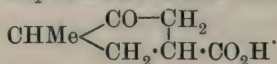
When finely divided sodium reacts with ethyl pentane- $\alpha\beta\delta$ -tricarboxylate under the conditions described on p. 768, a good yield of a keto-ester is obtained, which distils at 156—158°/12 mm.:

0.1582 gave 0.3449 CO_2 and 0.1105 H_2O . $\text{C}=59.5$; $\text{H}=7.7$.

$\text{C}_{12}\text{H}_{18}\text{O}_5$ requires $\text{C}=59.5$; $\text{H}=7.4$ per cent.

Ethyl 1-methylcyclopentan-2-one-3:4-dicarboxylate is a colourless oil, which is soluble in dilute alkalis and in sodium carbonate, and is reprecipitated by acids. Its alcoholic solution gives, on the addition of ferric chloride, an intense purple coloration. The semicarbazone separated under the usual conditions as a viscid syrup, which showed no signs of crystallising after remaining for a week in the ice-chest.

1-Methylcyclopentan-2-one-4-carboxylic Acid,



This acid was obtained when ethyl 1-methylcyclopentan-2-one-dicarboxylate was hydrolysed by boiling with 6 per cent. hydrochloric acid (compare p. 769); it distilled at 162—165°/12 mm. as a viscid, colourless syrup, which showed no signs of crystallising:

0.1879 gave 0.4044 CO_2 and 0.1206 H_2O . $\text{C}=58.7$; $\text{H}=7.1$.

$\text{C}_7\text{H}_{10}\text{O}_3$ requires $\text{C}=59.1$; $\text{H}=7.1$ per cent.

The *semicarbazone*, prepared in the usual way, separates from water as a crystalline powder, and melts and decomposes at 202—203°:

0.1178 gave 21.5 c.c. N_2 at 16° and 744 mm. $N=20.8$.

$C_8H_{13}O_3N_3$ requires $N=21.2$ per cent.

The *oxime* was obtained from the acid by treatment with hydroxylamine hydrochloride and potassium hydroxide, and, after acidifying, was extracted several times with considerable quantities of ether.

The ethereal solution deposited, on evaporation, a solid, which crystallised readily from ether, and melted and decomposed at 166—167°:

0.1243 gave 9.5 c.c. N_2 at 17° and 742 mm. $N=8.6$.

$C_7H_{11}O_3N$ requires $N=8.9$ per cent.

Ethyl 1-methylcyclopentan-2-one-4-carboxylate was obtained, by digesting the acid with 10 per cent. alcoholic sulphuric acid, as a colourless oil, which distilled at 115—117°/14 mm., and had a characteristic and pleasant odour:

0.1609 gave 0.3719 CO_2 and 0.1211 H_2O . $C=63.0$; $H=8.3$.

$C_9H_{14}O_3$ requires $C=63.5$; $H=8.3$ per cent.

The *semicarbazone* of this ester crystallises readily from ether, and melts at 138—140°.

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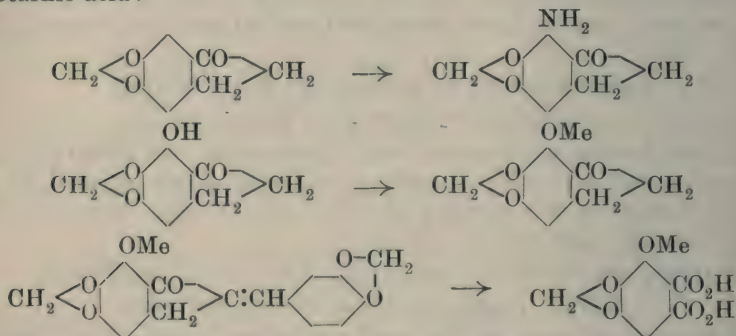
LXXXIII.—*Synthesis and Resolution of Gnoscopine (dl-Narcotine).*

By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

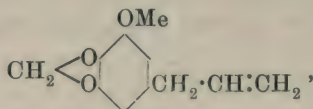
THE problem of the synthesis of alkaloids belonging to the *isoquinoline* group has engaged our attention for some years, and in the present communication we give an account of the final stages in the synthesis of narcotine, an alkaloid of particular importance, not only on account of its intrinsic chemical interest, but also because, next to morphine, it is the main constituent of opium. The mode of attack chosen was in accordance with the following scheme: (a) the synthesis of cotarnic acid, (b) the conversion of cotarnic acid into cotarnine, (c) the synthesis of gnoscopine

(*dl*-narcotine) from cotarnine, (*d*) the resolution of gnoscopine. The first stage in this scheme was accomplished in 1909 (Perkin, Robinson, and Thomas, *Trans.*, **95**, 1977).

The starting point in the synthesis of cotarnic acid was 5:6-methylenedioxy-1-hydrindone, which Perkin and Robinson had synthesised in 1907 (*Trans.*, **91**, 1084), and this was nitrated, the nitro-group reduced, replaced by hydroxyl, and then methylated. Lastly, the 7-methoxy-5:6-methylenedioxy-1-hydrindone was condensed with piperonal, and the product oxidised, when it yielded cotarnic acid:



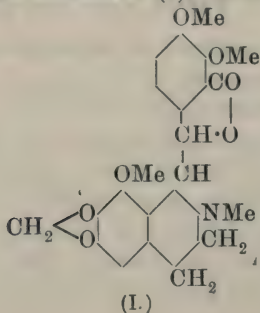
The second stage, namely, the synthesis of cotarnine, has recently been accomplished by Salway (*Trans.*, 1910, **97**, 1208) from myristicin,

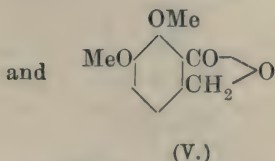
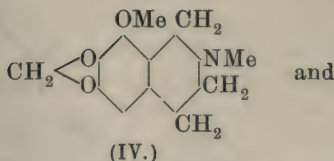
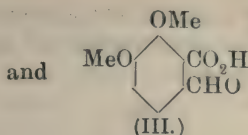
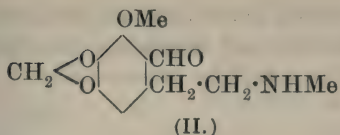


by a long series of reactions which cannot be given in detail here, and it therefore became unnecessary for us to continue our experiments in this direction.

The line of argument which we adopted in our experiments on the synthesis of gnoscopine was briefly as follows.

It is well known that narcotine (I), on oxidation, suffers fission

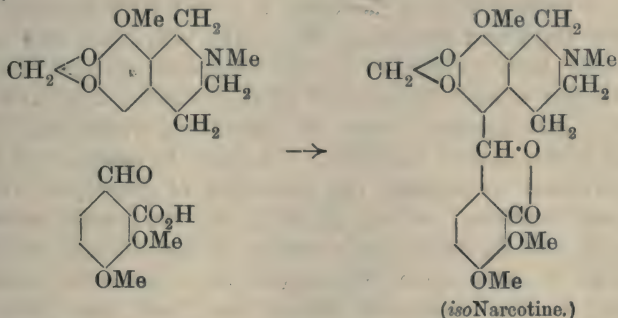




into cotarnine (II) and opianic acid (III); also that, on vigorous reduction, a somewhat similar decomposition occurs, and hydrocotarnine (IV) and meconine (V) are produced.

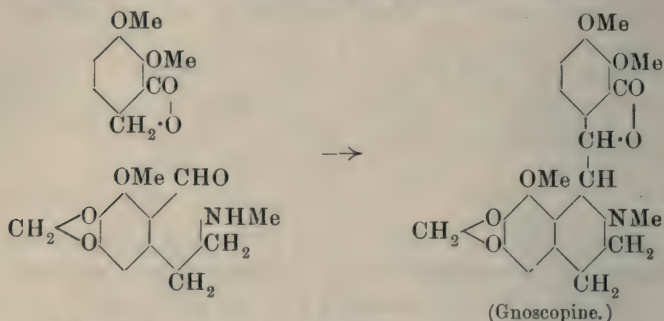
A consideration of the constitution of narcotine seemed to suggest that direct combination of the two parts of the molecule might be effected by causing the pairs, opianic acid and hydrocotarnine or cotarnine and meconine, to condense, either directly or indirectly.

Both these condensations have been investigated by Liebermann (*Ber.*, 1896, **29**, 180; 1904, **37**, 211), and whereas a negative result was obtained in the case of cotarnine and meconine, the reaction between opianic acid and hydrocotarnine resulted in the production of a new alkaloid—*isonarcotine*—which is distinguished from narcotine by its melting point (194°) and by the fact that it dissolves in sulphuric acid with a red coloration, whereas narcotine melts at 176° ; and dissolves in sulphuric acid, with the formation of a greenish-yellow solution. We have little doubt that this interesting substance, with the investigation of which we are at present actively engaged, is produced according to the following scheme:



and the fact that the condensation appears to take this course made it improbable that results of any value, so far as the synthesis of gnoscopine was concerned, would result from investigating this reaction under modified conditions. On the other hand, it was

thought possible that a synthesis of gnoscopine might result from the direct combination of cotarnine and meconine, provided that the exact experimental conditions could be determined:



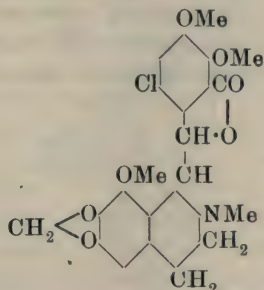
After a large number of fruitless experiments with sodium ethoxide, potassium hydroxide, and other alkaline condensing agents had been made, we succeeded at last in obtaining small quantities of gnoscopine by treating the alcoholic solution of cotarnine and meconine with potassium carbonate, and a short account of this synthesis has already appeared (*Proc.*, 1910, **26**, 46). It was subsequently discovered that a condensing agent is not only not necessary, but actually a disadvantage, and that gnoscopine is produced, although still in small quantities, when cotarnine and meconine are simply boiled together in alcoholic solution. The alkaloid obtained in these synthetical experiments was carefully compared with a specimen of gnoscopine from opium kindly sent us by Messrs. T. and H. Smith—the discoverers of gnoscopine—and it was at once seen that the two preparations were identical. That gnoscopine is *dl*-narcotine is shown by the fact that it is produced when narcotine is boiled with aqueous alcohol (compare Rabe and McMillan, *Ber.*, 1910, **43**, 800), and we have also found that gnoscopine yields cotarnine, opianic acid, and teropiammon when it is oxidised by dilute nitric acid, and can be converted into narceine under the conditions which lead to these changes in the case of narcotine. In order to complete the proof, we determined to attempt the resolution of gnoscopine (compare Rabe and McMillan, *loc. cit.*, p. 803), and are greatly indebted to Messrs. T. and H. Smith for a supply of this alkaloid sufficient to enable us to carry these experiments to a successful issue. The difficulty in this resolution lies in the fact that the salts of gnoscopine and narcotine are, generally speaking, badly characterised, and not suitable for fractional crystallisation. Ultimately we succeeded in fractionally crystallising the *d*-bromocamphorsulphonate, when the first crops of crystals proved to consist in the main of the *d*-bromocamphorsulphonate of *l*-narcotine, and from the pure

salt we obtained a specimen of *l*-narcotine which had $[\alpha]_D -199.8^\circ$, and was identical in all respects with the natural alkaloid from opium.

The mother liquor deposited a mixture of *d*-narcotine and gnoscopine *d*-bromocamphorsulphonates, and we were unsuccessful in separating these salts, but, when the bases were liberated, no difficulty was experienced in separating the *d*-narcotine and gnoscopine by recrystallisation from alcohol. *d*-Narcotine, which had not previously been obtained, was found to melt at $174-175^\circ$, to have $[\alpha]_D +199.9^\circ$, and to be identical in all its properties with the enantiomorphously-related *l*-narcotine; furthermore, when the hot alcoholic solutions of *d*- and *l*-narcotine were mixed, crystals of gnoscopine, melting at 230° , separated at once. A second series of experiments with *l*-bromocamphorsulphonic acid, for a supply of which, and also of the *d*-acid, we are indebted to Professor W. J. Pope, gave similar results; the salt which first separated was the salt of *d*-narcotine and from this pure *d*-narcotine was obtained, with properties exactly resembling those of the natural levorotatory alkaloid. Full details of these resolution experiments are given on pp. 788, 790.

The principal difficulty experienced in the course of the synthetic experiments just described is the smallness of the yield of alkaloid obtained during the condensation of meconine and cotarnine, and, although the conditions of experiment were varied in a great many directions, little or no improvement could be observed.

Recently, however, Hope and Robinson (Proc., 1910, **26**, 228) have shown that the introduction of the nitro-group into meconine enormously facilitates the ease with which that substance condenses with cotarnine, and, indeed, the yield of nitrognoscopine obtained by the interaction of nitromeconine and cotarnine is practically quantitative. We have found that the replacement of hydrogen in meconine by the halogens produces a similar effect; thus the yield of *chlorognoscopine* (m. p. 187°):

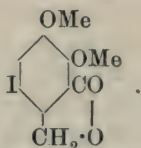


obtained when chloromeconine and cotarnine are boiled together

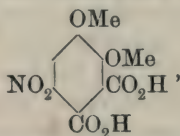
in methyl-alcoholic solution is much better than the yield of gnoscopine produced from meconine and cotarnine under the same conditions.

Bromomeconine and cotarnine give a still better yield of *bromognoscopine* (m. p. 188—189°), and, in the case of iodomeconine and cotarnine, the amount of *iodognoscopine* (m. p. 170°) produced is 50 per cent. of that theoretically possible.

These synthetical experiments have necessitated the careful repetition of Anderson's experiments (*Annalen*, 1860, **98**, 47) on the action of halogens on meconine, and there can be no doubt that, in all cases, the halogen replaces the hydrogen atom next the lactone group, and that iodomeconine, for example, has the formula:

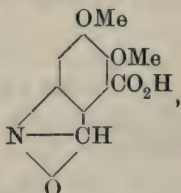


That this is the constitution of the iodomeconine (m. p. 134°) produced when meconine is treated with iodine chloride is proved by the formation of the same substance from nitromeconine by the following series of reactions. Nitromeconine is readily reduced by tin and hydrochloric acid, and when the product is diazotised and treated with potassium iodide, a substance is formed which melts at 124°, and is identical with the iodomeconine produced by direct substitution. When nitromeconine is oxidised with permanganate, it yields the nitrohemipinic acid:



which is also obtained by the oxidation of nitro-opianic acid.

That the nitro-group in nitro-opianic acid is in the ortho-position with respect to the aldehyde group is shown by the production of the internal anhydride, azo-opianic acid (Prinz, *J. pr. Chem.*, 1881, [ii], **24**, 362), probably an anthranil derivative:



by reduction with stannous chloride and hydrochloric acid.

It seems clear from this argument that the iodine in iodomeconine must occupy the ortho-position with respect to the lactonic group, and therefore have the constitution assigned to it above.

Experiments on the synthesis of *dl*-hydrastine by the condensation of hydrastinine with meconine are in progress, but the experimental conditions seem to be more difficult to determine than those necessary in the case of the condensation of meconine and cotarnine.

EXPERIMENTAL.

Synthesis of Gnoscopine.

It has already been stated in the introduction that a large number of experiments on the action of powerful condensing agents, such as sodium ethoxide, potassium hydroxide, diethylamine, and piperidine, on mixtures of cotarnine and meconine, failed to yield gnoscopine, and we now give a short account of those experiments which led to a successful issue.

I. *Condensation of Cotarnine with Meconine in the Presence of Potassium Carbonate.*—Meconine (20 grams) was dissolved in alcohol (100 c.c.), and to the boiling solution cotarnine (20 grams) was added, together with anhydrous potassium carbonate (20 grams). The mixture was boiled on the steam-bath for four hours, during which time the alcohol acquired a deep yellowish-red colour. The solution was filtered from excess of potassium carbonate, diluted with water, and the brownish-yellow, viscid oil which separated removed from the mother liquor by decantation, when it was noticed that the latter, on keeping, deposited crystals of meconine.

The oil was washed with water, and treated with dilute hydrochloric acid, in which it was completely soluble, the yellow solution was warmed with a little purified animal charcoal, filtered, and mixed with excess of mercuric chloride solution. The nearly colourless mercurichloride, which was precipitated in considerable quantity, was collected, and it had then all the appearance of the mercurichloride of narcotine. It was dissolved in hot dilute hydrochloric acid, and the mercury removed by hydrogen sulphide, when an almost colourless solution was obtained, which yielded precipitates with alkaloidal reagents, very closely resembling those obtained with narcotine solutions. The base, liberated by the addition of ammonia, separated, however, in flocks, and could not be induced to crystallise; it was therefore purified by a second treatment with mercuric chloride. The precipitation in this case was carried out fractionally, and the first portion, which was obviously less pure than the rest, was rejected.

The double compound was again decomposed by hydrochloric

acid and hydrogen sulphide, and the fractional precipitation with mercuric chloride repeated; finally, the base was precipitated with sodium carbonate and extracted with ether. The ethereal solution was washed with water, dried over potassium carbonate, evaporated to a small bulk, and left in the ice-chest for some weeks, when small prisms separated, which were collected, and, after crystallisation from alcohol, found to consist of pure gnoscopine.

II. *Condensation of Cotarnine with Meconine without a Condensing Agent. First Experiment.*—Cotarnine (5 grams) and meconine (5 grams) were boiled in methyl alcohol (30 c.c.) for six and a-half hours on the steam-bath. When the orange-yellow product was poured into water, and the whole allowed to remain, a sticky oil was deposited, which was separated from the clear aqueous solution by decantation, washed with water, and dissolved in a slight excess of dilute hydrochloric acid. A small quantity of a solid which remained undissolved was removed by filtration, and found to consist of meconine. The addition of excess of sodium acetate to the filtrate caused the precipitation of a base which, on account of its sticky nature, could be easily collected on a glass rod. The substance was then well washed with water, and dried by keeping the glass rod in a vacuum over sulphuric acid. It was then dissolved in methyl alcohol, and the solution concentrated, when, on long keeping, a quantity of needle-shaped crystals separated, which were collected, recrystallised from methyl alcohol, and found to consist of pure gnoscopine.

Second Experiment.—This experiment was made with the same quantities, and the solution was kept at the ordinary temperature for one month, when most of the meconine dissolved, and the solution acquired a yellow colour. The process of isolation and purification was the same as that adopted in the first experiment, and resulted again in the isolation of small quantities of pure gnoscopine.

In the case of all the condensations described above, the alkaloid was obtained in colourless needles very sparingly soluble in methyl alcohol, and melting at 229° . Not only did the synthetical substance show exactly the same crystalline form as gnoscopine and yield exactly the same derivatives, but, when mixed with a very pure sample of gnoscopine, presented to us by Messrs. T. and H. Smith, the mixture melted at the same temperature as the constituents.

The *picrate* was found to be readily formed by adding a solution of picric acid in methyl alcohol to a solution of gnoscopine in methyl ethyl ketone, and crystallised in beautiful, yellow prisms, which melted at $188\text{--}189^{\circ}$. The *platinichloride*, *mercurichloride*,

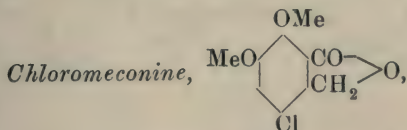
and *aurichloride* are pale yellow, colourless, and buff precipitates respectively, and, although amorphous, are yet characteristic and exactly similar to the precipitates produced with the natural alkaloid.

Gnoscopine Methiodide.—This derivative has already been described by Frerichs (*Arch. Pharm.*, 1903, **241**, 268), and by Rabe and McMillan (*Ber.*, 1910, **43**, 802). We find that it possesses the characteristic property of crystallising with two molecules of water in magnificent prisms. On exposure in a vacuum desiccator over sulphuric acid or phosphoric oxide, these crystals fall to a powder of the anhydrous methiodide:

1.405 lost 0.0801 H₂O. H₂O=5.7.

C₂₂H₂₃O₇N, MeI, 2H₂O requires H₂O=6.1 per cent.

The anhydrous methiodide was found to melt at 210—212°, and to decompose at a slightly higher temperature. It was converted into narceine by the method described for the conversion of narcotine into this substance. The narceine obtained melted at 172—175°, and had the other properties of a specimen of narceine which had been extracted from opium by Messrs. T. and H. Smith.



Bromomeconine, and Iodomeconine.

These substances have been prepared in considerable quantities for use in the synthesis of halogen derivatives of gnoscopine.

Chloromeconine has been described by Anderson (*Annalen*, 1860, **98**, 47), who prepared it by passing chlorine into a cold aqueous solution of meconine, and states that it crystallises in needles and melts at 175°.

We find that it is preferable to pass chlorine into the solution of meconine in glacial acetic acid, when the chloro-derivative separates in crystals, and is readily purified by recrystallisation from glacial acetic acid. It is very sparingly soluble in alcohol, and melts at 183°.

Bromomeconine has also been described by Anderson (*loc. cit.*, p. 48), who states that it melts at 167°, and by Salomon (*Ber.*, 1887, **20**, 888), who gives 177° as the melting point. The method we have found convenient for its preparation is the following. Meconine (20 grams) was dissolved in warm glacial acetic acid (50 c.c.), and then gradually mixed with bromine (17 grams). The solution was allowed to remain until the colour became pale orange;

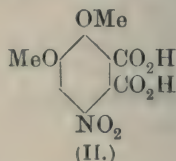
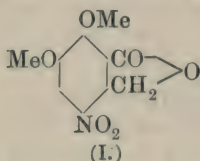
it was then mixed with about a quarter of its volume of water, and cooled. The bromomeconine which separated was collected, and crystallised from alcohol, from which it separated in needles, melting at 176° .

Iodomeconine, which has been mentioned by Anderson (*loc. cit.*), who gives 112° as the melting point, was prepared in the following way. Meconine (10 grams) was dissolved in glacial acetic acid (40 c.c.), the solution heated to boiling, and gradually mixed with iodine monochloride (15 grams), when evolution of hydrogen chloride took place. After a few minutes, a little water was added, and the excess of iodine removed by passing sulphur dioxide. The iodomeconine was then precipitated by water, and the yellow solid collected and crystallised from alcohol, from which it separated in needles, which gradually changed to prisms. The melting point is 124° :

0.1551 gave 0.1130 AgI. $I = 39.4$.

$C_{10}H_9O_4I$ requires $I = 39.7$ per cent.

The constitution of iodomeconine is proved by the fact that we have succeeded in obtaining it from nitromeconine (I).

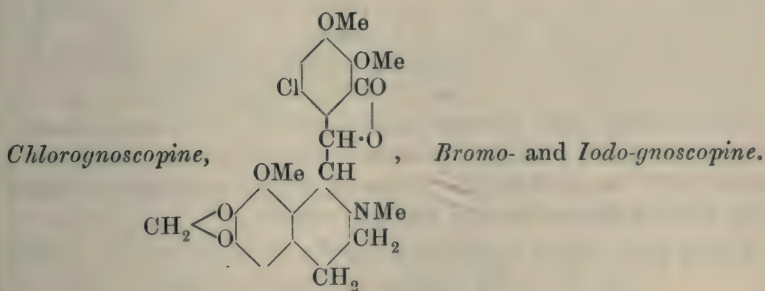


This substance was prepared by the action of nitric acid on meconine, essentially according to the method described by Anderson (*Annalen*, 1860, **98**, 46), and its constitution was proved by oxidation with permanganate, when it yields the nitrohemipinic acid of the formula (II).

Preparation of Iodomeconine from Nitromeconine.—Nitromeconine (5 grams) was reduced with tin and hydrochloric acid (50 c.c.), and when the whole of the substance had dissolved, the pale yellow solution was decanted from the excess of tin. Zinc was now added to eliminate the tin, and the viscid solution diluted with about 100 c.c. of water. The amino-compound was then diazotised, and the solution poured into potassium iodide (20 grams) dissolved in about 200 c.c. of water. Nitrogen was immediately evolved, a dark-coloured solid separated, and, after passing sulphur dioxide to remove free iodine, the solid was collected, washed, and crystallised from alcohol, from which it separated in needles, melting at 124° . That this substance is identical with the iodomeconine obtained by direct substitution was shown by careful comparison of the properties, and by the fact that a mixture of the two prepara-

tions melted at 124° . It is clear therefore that the iodine atom in iodomeconine occupies the same position as does the nitro-group in nitromeconine.

Oxidation of Nitromeconine to Nitrohemipinic Acid.—Nitromeconine (2 grams) was dissolved in as little hot dilute potassium hydroxide as possible, the solution diluted with water, warmed on the steam-bath, and potassium permanganate added until the pink colour remained permanent. The excess was destroyed with alcohol, the solution filtered from the manganese precipitate, and somewhat concentrated. An excess of ammonia and barium chloride was then added, and the voluminous, yellow barium salt, which separated in needles, was collected, washed, and warmed with a little hot dilute sulphuric acid. The filtrate from the barium sulphate was saturated with hydrogen chloride, when needles of nitrohemipinic acid separated, and, after drying, this acid was converted into the anhydride by heating. After crystallisation from benzene, this anhydride melted at 150 — 151° , and was identical with a specimen of the same substance prepared from nitro-opiatic acid by oxidation, a fact which proves conclusively that this nitrohemipinic acid has the constitution assigned to it above (compare p. 780).



The synthesis of chlorognoscopine was accomplished under the following conditions. Finely powdered chloromeconine (10 grams) was boiled with sufficient methyl alcohol to dissolve all but a very small residue; cotarnine (6 grams) was then added, and the boiling continued in a reflux apparatus for three hours. The orange solution was cooled and treated with excess of dilute hydrochloric acid, the pale yellow liquid was filtered from some unchanged chloromeconine, and the base set free with ammonia. The sticky substance which separated became hard and crystalline when washed with water, and was then crystallised, first from methyl alcohol, and then from ethyl alcohol. It is very sparingly soluble

in the former solvent, rather more so in the latter, and separates in beautiful, glistening, prismatic needles, which are quite colourless, and melt at 187° . For analysis, the substance was dried over sulphuric acid in a vacuum desiccator:

0.1202 gave 0.0389 AgCl. $\text{Cl}=7.9$.

$\text{C}_{22}\text{H}_{22}\text{O}_7\text{NCl}$ requires $\text{Cl}=7.8$ per cent.

Chlorognoscopine is readily soluble in dilute aqueous acids, and the properties of its salts and double salts are practically the same as those of the corresponding salts of gnoscopine. A blood-red coloration is developed on the addition of a trace of nitric acid to the solution of the substance in concentrated sulphuric acid.

The *picrate* is produced by mixing hot solutions of chlorognoscopine and picric acid in methyl ethyl ketone, and separates, on cooling, in lemon-yellow needles. It is sparingly soluble in hot alcohol and in cold methyl ethyl ketone, and melts at about 201° .

Bromognoscopine.—In preparing this substance, a mixture of bromomeconine (15 grams), cotarnine (10 grams), and methyl alcohol (65 c.c.) was boiled in a reflux apparatus for one and a-half hours, when the greater part of the bromomeconine passed into solution.

Water was added, the solution rendered acid by the addition of hydrochloric acid, and the clear yellow filtrate from unchanged bromomeconine was mixed with excess of sodium acetate. The pale yellow, amorphous precipitate, which gradually became crystalline, was collected, extracted with a small quantity of hot methyl alcohol, and the residue crystallised from ethyl alcohol. Bromognoscopine separates in small, shining prisms, which melt at 188 — 189° to a red liquid. For analysis, the substance was dried in a vacuum desiccator over sulphuric acid:

0.1633 gave 0.0624 AgBr. $\text{Br}=16.3$.

$\text{C}_{22}\text{H}_{22}\text{O}_7\text{NBr}$ requires $\text{Br}=16.3$ per cent.

Bromognoscopine is sparingly soluble in ether or methyl or ethyl alcohols, moderately so in benzene or ethyl acetate, and readily so in chloroform. It dissolves readily in dilute acids, forming colourless solutions. The *mercurichloride* is a white, amorphous precipitate, the *platinichloride* is nearly colourless and sparingly soluble, whilst the *aurichloride* is produced in very dilute solutions as a pale yellow precipitate. The *picrate* of bromognoscopine is a canary-yellow substance, which may be crystallised by adding methyl alcohol to its solution in methyl ethyl ketone, when it separates in prisms, melting at 206° .

Iodognoscopine.—The condensation between cotarnine and iodomeconine occurs more readily than that between cotarnine and chloromeconine or bromomeconine, and, although the yield is not so good as in the case of the corresponding nitro-compound (Hope and Robinson, Proc., 1910, **26**, 228), yet, in favourable circumstances, as much as 50 per cent. of the theoretical yield has been obtained. In preparing this substance, the following conditions were ultimately found to give the most satisfactory results. Iodomeconine (4 grams) and cotarnine (3 grams) are boiled together in methyl-alcoholic solution in a reflux apparatus for four hours. The addition of water to the deep red solution causes the separation of an orange, oily precipitate, and, after keeping, the clear supernatant liquid is decanted and the sticky mass washed with water, and finally treated with dilute acetic acid.

Most of the substance dissolves, leaving iodomeconine in the crystalline condition; this is collected, and the base liberated from the filtrate by ammonia and dissolved in methyl alcohol. The substance dissolves readily in the cold, but, on keeping in the ice-chest, and especially if a crystal from a previous preparation has been added, a quantity of crystals gradually separate.* These are collected and recrystallised from alcohol, from which *iodognoscopine* separates in beautiful, colourless prisms, melting at 170°:

0.1270 gave 0.0550 AgI. $I = 23.4$.

$C_{22}H_{22}O_7NI$ requires $I = 23.3$ per cent.

Iodognoscopine Methiodide.—In preparing this derivative, iodognoscopine was boiled, in a reflux apparatus, with an excess of methyl iodide (free from iodine) during two hours. The excess of methyl iodide was distilled off, and the residue crystallised from methyl alcohol, from which iodognoscopine methiodide separates in stout, pale yellow prisms, melting at 190—195°.

This substance is soluble in much boiling water, and crystallises on cooling. It is converted by freshly precipitated silver chloride into the correspondingly readily soluble methochloride, and, on the addition of alkali to the filtrate from the silver iodide, an amorphous precipitate of a methyl hydroxide is produced. This precipitate

* When the substance has once been obtained in a crystalline condition, the best procedure is to seed the original methyl-alcoholic solution of the products of condensation of iodomeconine and cotarnine. This causes iodognoscopine, mixed with iodomeconine, to crystallise out; the separation of these two substances is readily effected by means of dilute acid and the regenerated base does not need recrystallising.

was collected and boiled with a large excess of water, in the hope that an idonarceine would result. It is strange, however, that in this instance, the reaction seems to follow a different course.

The greater portion of the methyl hydroxide remained undissolved, and the aqueous solution, on concentration, deposited only a small quantity of a substance which crystallised in brilliant, satiny spangles, and melted and decomposed at 240°. This substance has basic properties, and contains iodine, but it behaves differently from a narceine, in that it gives no colour with iodine or with chlorine water and ammonia; a cherry-red colour is, however, developed by warming on the water-bath with 50 per cent. sulphuric acid. It is soluble in sodium hydroxide, but not in sodium carbonate. The poor yield of this substance obtained from iodognoscopine did not allow of further investigation.

Resolution of Gnoscopine into d- and l-Narcotine.

Among the many experiments carried out in connexion with this resolution, the following may be described in detail:

I. *Resolution with the aid of d-Bromocamphorsulphonic Acid.*—Ammonium *d*-bromocamphorsulphonate (31 grams) was boiled in aqueous solution with barium hydroxide (9 grams) until the evolution of ammonia had ceased; the barium was then exactly precipitated with sulphuric acid, and the filtered solution boiled with finely powdered gnoscopine (44 grams). Most of the gnoscopine passed into solution, and care was taken to use sufficient water to prevent the alkaloid salt from separating as a sticky mass. When the filtered solution was allowed to cool, the salt separated as an oil, which, however, solidified on keeping in the ice-chest for several days, and also a quantity of salt crystallised from the solution. No resolution was effected by this process, as a sample of the salt yielded pure gnoscopine on decomposition with ammonia. The crystalline cake and the crystals from the solution were collected, carefully dried in a vacuum, and then many experiments were tried with the object of recrystallising the salt from a neutral solvent, but for a long time without success.

Ultimately a crystal was obtained as a single nucleus in a gum which resulted from the slow evaporation of the solution of the salt in acetone. This was used to seed a very concentrated solution of the salt in ethyl acetate, and finally the whole mass of the salt was crystallised from a small quantity of ethyl acetate. The salt which separated was collected, washed with a little very cold ethyl acetate, and recrystallised three times from this solvent.

Since further recrystallisation did not alter its properties, this salt was considered pure; it is very soluble in alcohol or ethyl acetate, and crystallises in long, slender needles, which felt together.

When dried over sulphuric acid in a vacuum desiccator, it melts at 110—120°, with evolution of gas, but the air-dried salt melts at about 80—90°.

The analysis of the air-dried substance gave the following results:

0.1200 gave 0.0282 AgBr. Br=10.0.

$C_{22}H_{23}O_7N, C_{10}H_{15}O_4BrS, Me \cdot CO_2Et$ requires Br=9.8 per cent.

That this salt contained ethyl acetate was proved by the odour of this substance, which was at once evident when the salt was boiled with water. Experiment showed that this salt is markedly dextrorotatory, since 0.4497, made up to 20 c.c. with chloroform, gave, in a 2-dcm. tube, $\alpha + 4.5^\circ$, whence $[\alpha]_D + 100.7^\circ$.

That this salt is *l*-narcotine *d*-bromocamphorsulphonate was proved by the fact that its alcoholic solution, on the addition of a few drops of ammonia, yields an excellent crop of crystals of *l*-narcotine, identical in all respects with narcotine from opium. The *l*-narcotine obtained from the salt was recrystallised once from ethyl alcohol, from which it separated in colourless needles, melting at 175°.

This was found to be the melting point of a specimen of pure narcotine from opium, for which we are indebted to Messrs. T. and H. Smith, and, furthermore, a mixture of the two preparations melted at the same temperature as the constituents. The following comparative determinations of specific rotation demonstrate the high degree of purity of the *l*-narcotine obtained from gnoscopine.

0.6712 of *l*-narcotine, from opium, made up to 20 c.c. with chloroform, gave, in a 2-dcm. tube, $\alpha - 13.42^\circ$, whence $[\alpha]_D - 199.85^\circ$.

0.3953 of *l*-narcotine, from gnoscopine, made up to 20 c.c. with chloroform, gave, in a 2-dcm. tube, $\alpha - 7.9^\circ$, whence $[\alpha]_D - 199.84^\circ$.

The mother liquor from the salt, *l*-base-*d*-acid, deposited three further crops of crystals, *A*, *B*, and *C*. The crop *A* was considerable in quantity but very different in appearance from the salt, *l*-base-*d*-acid.

It was crystallised from ethyl acetate, in which it is more sparingly soluble than the latter, and was obtained in prisms melting at 170—185°:

0.1025 gave 0.0260 AgBr. Br=10.8.

$C_{22}H_{23}O_7N, C_{10}H_{15}O_4BrS$ requires Br=11.0 per cent.

This salt is *d*-narcotine *d*-bromocamphorsulphonate, mixed with

the corresponding gnoscopine salt, since when decomposed with ammonia it yields the hitherto unknown *d*-narcotine mixed with gnoscopine.

The salt was dissolved in alcohol and decomposed by the addition of a few drops of ammonia, the solution heated to boiling, and filtered.

The residue, after crystallisation from alcohol, melted at 228° , and consisted of pure gnoscopine, and the filtrate deposited a large quantity of needle-shaped crystals exactly resembling ordinary *l*-narcotine in appearance. After recrystallisation from alcohol, the substance melted at 175° , and the determination of the specific rotation clearly showed that it is pure *d*-narcotine, the enantiomorph of ordinary *l*-narcotine. 0.5212, made up to 20 c.c. with chloroform, gave, in a 2-dcm. tube, $\alpha + 10.42^{\circ}$, whence $[\alpha]_D + 199.92^{\circ}$.

When hot alcoholic solutions of *d*- and *l*-narcotine are mixed, the very much less soluble *dl*-narcotine (gnoscopine) crystallises immediately from the solution, and exhibits at once the correct melting point 228° .

This great difference in solubility makes the separation of narcotine from gnoscopine an easy matter. Thus, for example, when 0.5 gram of narcotine was mixed with 2 grams of gnoscopine and the mixture crystallised once from alcohol, an almost complete separation was accomplished. In resolution experiments, such as those described above, it is therefore not essential to achieve a complete separation of the salts. Crop *B* melted at 160 – 180° , and, after conversion into the bases in the manner described in the case of *A*, yielded, on crystallisation from alcohol, about 2 grams of gnoscopine and 1 gram of *d*-narcotine. Crop *C* melted at about 190° , and gave on decomposition with ammonia almost pure gnoscopine. The alcoholic filtrate from the crystallisation of the gnoscopine, after acidifying with hydrochloric acid, was found to be slightly lævorotatory, and this indicates the presence of *d*-narcotine, since *l*-narcotine is dextrorotatory in acid solution.

The amount of the salt of *d*-narcotine present in this fraction *C* must, however, have been very small. The analysis of the crystals of crop *C* gave the following results:

0.1183 gave 0.0297 AgBr. Br = 10.7.

$C_{32}H_{38}O_{11}NBrS$ requires Br = 11.0 per cent.

0.4310, made up to 20 c.c. with chloroform, gave, in a 2-dcm. tube, $\alpha + 0.87^{\circ}$, whence $[\alpha]_D + 20.2^{\circ}$. It is probable that this *dl*-salt may not be crystallisable, without resolution, when it is quite pure, and that the slight excess of the salt of the *d*-base

contained in the solution prevents the formation of a crystal of the salt of the *l*-base, and makes the separation of a crystal of the salt, *dl*-base-*d*-acid, possible. We found, for example, that the addition of 0.5 gram of *l*-base-*d*-acid to the cooled solution of the gnoscopine *d*-bromocamphorsulphonate in ethyl acetate caused the separation of about 2 grams of the salt of the *l*-base.

II. *Resolution with the aid of l-Bromocamphorsulphonic Acid.*—This resolution was attempted in order to obtain a sufficient supply of *d*-narcotine for physiological investigation.

Gnoscopine (20 grams) was boiled with an aqueous solution of *l*-bromocamphorsulphonic acid (12 grams) until as much as possible had dissolved; the unchanged alkaloid was separated by filtration, and the solution concentrated to half its bulk. The oil, which separated on cooling, gradually solidified, and was ultimately obtained as a crystalline cake; this was dissolved in a small quantity of ethyl acetate, and allowed to remain in the ice-chest until crystallisation commenced. As soon as this occurred, the solution was diluted with about half its volume of ethyl acetate, and allowed to remain in the cold place.

The character of the crystals which separated was similar to that of the first crop from the resolution with the *d*-acid and the salt, which is pure *d*-narcotine *l*-bromocamphorsulphonate melts, after exposure to the air until dry, at 80—90°.

0.6638, made up to 20 c.c. with chloroform, gave, in a 2-dcm. tube, $\alpha - 6.45^\circ$, whence $[\alpha]_D - 97.2^\circ$. The *d*-narcotine obtained from the salt by means of ammonia melted at 175°, and had $[\alpha]_D + 199.8^\circ$.

The mother liquor from the *d*-base-*l*-acid salt gave, on exposure to the air, two further crops, *A* and *B*, neither of which were quite pure. *A* consisted chiefly of the salt, *l*-base-*l*-acid, and, on recrystallisation from ethyl acetate, was obtained in hard, colourless prisms, melting at 180—185°.

0.1202 gave 0.0299 AgBr. Br=10.6.

$C_{32}H_{38}O_{11}NBrS$ requires Br=11.0.

0.5325, made up to 20 c.c. with chloroform, gave, in a 2-dcm. tube, $\alpha + 1.55^\circ$, whence $[\alpha]_D + 29.01^\circ$. The *l*-narcotine obtained from this salt melted after recrystallisation at 175°, and gave pure gnoscopine (m. p. 228°) when mixed with *d*-narcotine in alcoholic solution.

The crop *B* melted at 180—190°, and consisted chiefly of gnoscopine *l*-bromocamphorsulphonate, mixed with a little *l*-narcotine salt.

The bases set free from these salts were easily separated by crystallisation from alcohol in the manner previously described (p. 790).

In concluding our experiments we have also prepared *dl*-narcotine *dl*-bromocamphorsulphonate, for the reason that we wished to be certain that the active salts, obtained during the course of the two series of resolutions just described, were true enantiomorphs.

We have obtained this salt by mixing the following pairs of salts in ethyl acetate solution:

- (a) *l*-base-*d*-acid and *d*-base-*l*-acid.
- (b) *l*-base-*l*-acid „ *d*-base-*d*-acid.
- (c) *dl*-base-*l*-acid „ *dl*-base-*d*-acid.

This salt is more sparingly soluble in ethyl acetate than any of the other salts described in this paper, and crystallises in colourless prisms, melting at 189°:

0.1312 gave 0.0345 AgBr. Br=11.2.

$C_{32}H_{38}O_{11}NBrS$ requires Br=11.0 per cent.

That this salt is inactive was confirmed by direct observation.

We wish, in conclusion, to say that we are greatly indebted to the Research Fund of the Royal Society for a grant in aid of the expenses of this research.

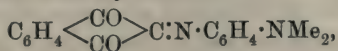
THE UNIVERSITY,
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LXXXIV.—*Triketohydrindene Hydrate. Part III. Its Relation to Alloxan.*

By SIEGFRIED RUHEMANN.

THE preparation of triketohydrindene hydrate (Trans., 1910, 97, 1438) from α -hydrindone is a very troublesome task, especially if a large quantity of the substance is required; it therefore became desirable to produce it by a more expedient method. With this object, attempts have been made to prepare the triketone from 1-3-diketohydrindene, since this compound is more readily obtainable

than α -hydrindone. The diketone, indeed, condenses with *p*-nitroso-dimethylaniline to yield dimethylaminoanilodiketohydrindene,

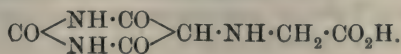


which, with dilute sulphuric acid, forms triketohydrindene hydrate, but the yield of the anilo-compound is unsatisfactory. Even less convenient for this purpose is β -hydrindone, because this substance can only be procured after considerably greater expenditure of time and trouble than α -hydrindone. After this experience, and owing to the fact that ether has to be used for extracting the triketone from the products of the action of mineral acids on the anilo-compounds, the first method of preparation of the triketone had to be adopted in order to obtain this substance for the continuation of the research.

It was stated previously (Trans., 1910, 97, 2025) that triketohydrindene hydrate gives a deep blue coloration with amino-acids, and it has since been found that it is a most valuable reagent for proteins and their hydrolytic products, since by means of it mere traces of those substances can be recognised. The isolation of the coloured products which are formed in the reaction presents great difficulties, and, as yet, has not been effected. The fact which has been established that their formation is accompanied by the production of aldehydes points to a similarity in the behaviour between triketohydrindene hydrate and alloxan.

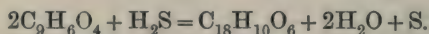
Strecker (*Annalen*, 1862, 123, 363) showed that, on warming aqueous solutions of a mixture of alloxan and an amino-acid, carbon dioxide is evolved, and, at the same time, aldehydes and murexide are produced. Alloxan, therefore, reacts in these cases as an oxidising agent, and transforms alanine into acetaldehyde, and leucine into valeraldehyde. On using glycine, Strecker was unable to prove the formation of formaldehyde, although, in other respects, the reaction proceeded in the same way as with the former amino-acids; he, therefore, concluded that the formaldehyde underwent oxidation to formic acid or carbon dioxide.

Piloty and Finckh (*Annalen*, 1904, 333, 68), in the course of their researches on the uric acid group, repeated Strecker's experiment concerning the action of alloxan on glycine, and arrived at the result that, along with uramil, a red-coloured compound was formed, which they regarded as the glycine salt of purpuric acid. This readily decomposed, yielding a brown, amorphous product and a substance which they considered to be uramiloacetic acid,



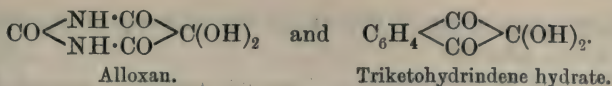
Recently Hurtley and Wootton (this vol., p. 288) studied the interaction of glycine and alloxan again; they state that form-aldehyde is evolved, and arrive at views concerning the other products of the reaction which differ from those of Piloty and Finckh.

The behaviour of triketohydrindene hydrate towards amino-acids is similar to that of alloxan; in this case, also, carbon dioxide is evolved and aldehydes are produced. This fact, together with the results of Strecker's experiments and those of Piloty and Finckh, seem to indicate that the blue coloration is preceded by the formation of a substance which resembles alloxantin. Such a compound is readily formed on treatment of the aqueous solutions of triketohydrindene hydrate with hydrogen sulphide, thus:



This substance may be called *hydrindantin*. It has properties which show a striking resemblance to alloxantin; it is colourless, even less soluble in water than alloxantin, and, like this compound, crystallises with two molecules of water. Of great interest is, first of all, the fact that it yields a blue coloration with amino-acids. This result supports the view expressed above concerning the chemical nature of the reaction which diketohydrindene hydrate gives with amino-acids. Hydrindantin, further, shows the following characteristic behaviour. It dissolves in cold sodium carbonate to form a deep red solution, from which it is precipitated unaltered on the addition of dilute hydrochloric acid. Another salt is produced on using sodium hydroxide (or potassium hydroxide) instead of the carbonate, and this is dark blue. Baryta water, also, gives a blue salt with hydrindantin, as it does with alloxantin. The behaviour of the blue salts of alloxantin and its analogue is alike; both are fairly stable towards heat, but lose their colour under the influence of oxygen. On passing the gas through the blue solution of hydrindantin in potassium hydroxide, the colour disappears in a short time, and the alkaline liquor then contains the salt of *o*-carboxymandelic acid, which, in turn, yields phthalidecarboxylic acid, $C_6H_4 \begin{array}{c} \text{CH}(\text{CO}_2\text{H}) \\ \text{CO} \end{array} \text{O}$. The acid is also produced by the action of the alkali on triketohydrindene hydrate (Trans., 1910, 97, 2025), and this fact leads to the view that the formation of the acid from hydrindantin is preceded by the production of the triketone.

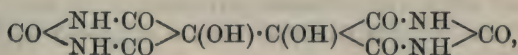
The close resemblance in the properties of triketohydrindene hydrate and alloxan finds its expression in the similarity of their formulæ:



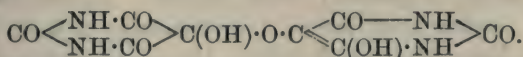
Piloty and Finckh (*loc. cit.*) draw the conclusion that, owing to the property of alloxan to form coloured derivatives with a quinonoid structure, it is itself a quinonoid compound. Hantzsch and Robison (*Ber.*, 1910, 43, 95) already pointed out that no sufficient evidence exists in support of this view. This follows, also, from the similarity of alloxan to triketohydrindene hydrate; the latter compound is colourless, because it does not contain the quinonoid grouping which is to be found in the diketopyrrolines and their analogues.

Constitution of Alloxantin and Hydrindantin.

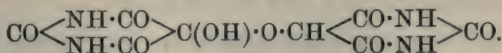
Piloty and Finckh (*loc. cit.*) have shown that the constitution of alloxantin,



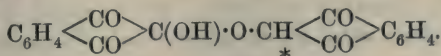
which was generally accepted, is unsatisfactory, and substitute for it the formula :



This they find to be in full agreement with the facts and to express the similarity which they consider to exist between alloxantin and quinhydrone; there is, however, no sufficient reason for such a comparison, nor is it necessary. Piloty and Finckh's formula which, on the whole, accounts for the behaviour of alloxantin, yet requires the following slight alteration :



This formula was suggested before by Slimmer and Stieglitz (*Amer. Chem. J.*, 1904, 31, 661); it characterises the substance as an alicyclic system which, as such, does not form salts. Indeed, alloxantin yields a violet barium compound, but its production, undoubtedly, is accompanied by a structural change. Accordingly, the constitution of hydrindantin is to be represented thus :



The formation of chromo-salts from hydrindantin and alloxantin may be explained by the change of the diketonic structure into the enolic-

ketonic grouping which is caused by the shifting of the hydrogen marked by an asterisk.

The formula of hydrindantin, however, does not account for the existence of two different sodium salts, namely, a red salt which the compound forms with sodium carbonate, and a blue salt which it yields with sodium hydroxide. Experiments are in progress with the object of arriving at an explanation of this phenomenon.

EXPERIMENTAL.

Formation of Triketohydrindene Hydrate from 1:3-Diketohydrindene and β -Hydrindone.

1:3-Diketohydrindene, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH_2$, was prepared by following Wislicenus and Kötze's directions (*Annalen*, 1889, 252, 72) for the production of ethyl sodio-diketohydrindenecarboxylate and then decomposing this compound in the manner suggested by Kaufmann (*Ber.*, 1897, 30, 385). The condensation of the diketone with sodio-*p*-nitrodimethylaniline takes place without the use of alkali, simply by mixing the reagents dissolved in hot alcohol. An ebullition occurs, the solution turning deep brown and depositing a dark solid; this dissolves in a large quantity of boiling alcohol to yield a deep violet solution and, on cooling, gradually separates in bluish-green needles, which melt and decompose at 211° . The compound, 2-Dimethylamino-anilo-1:3-diketohydrindene, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:N \cdot C_6H_4 \cdot NMe_2$, contains water of crystallisation which it loses, slowly, on drying in the air, but rapidly on heating in the water-oven; at the same time, the bluish-green crystals assume a deep bronze colour:

0.2012* gave 0.5405 CO_2 and 0.0930 H_2O . $C = 73.26$; $H = 5.13$.

0.2127 „ 19.2 c.c. N_2 at 20° and 748 mm. $N = 10.16$.

$C_{17}H_{14}O_2N_2$ requires $C = 73.38$; $H = 5.04$; $N = 10.07$ per cent.

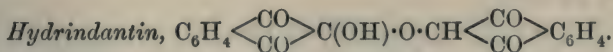
The yield of this substance is unsatisfactory, a large portion of the diketohydrindene being transformed into a black amorphous product which gradually separates from the mother-liquor of the greenish crystals; it readily dissolves in hot alcohol to form a deep red solution and, on cooling, is deposited as a resin. On digesting dimethylamino-anilodiketohydrindene with an excess of dilute sulphuric acid on the water-bath, it decomposes and yields triketohydrindene hydrate. This was isolated by frequent extractions of the dark liquor, which is

* Air-dried.

formed, with ether and, after crystallisation from water, was identified by analysis (Found: C = 60.59; H = 3.66. Calc., C = 60.67; H = 3.37 per cent.) and by its characteristic reactions.

β -Hydrindone may be transformed into triketohydrindene hydrate in the same way as α -hydrindone, and 1:3-diketohydrindene. For the preparation of β -hydrindone, Heusler and Schieffer's method (*Ber.*, 1899, 32, 28) was used, which gives a satisfactory yield, but is very troublesome. The hydrindone readily reacts with *p*-nitrosodimethylaniline on mixing the reagents dissolved in hot alcohol. The solid which separates is only sparingly soluble in alcohol or benzene, but moderately so in chloroform, yielding a deep red solution, from which, on cooling, bronze-coloured needles crystallise out, melting and decomposing at 214°. This substance was not analysed, but there can scarcely be any doubt that it is 1:3-bis(*p*-dimethylaminoanilo)

β -hydrindone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2) \\ \text{C}(\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2) \end{smallmatrix} > \text{CO}$, because it dissolves in dilute sulphuric acid, on warming, to form a dark solution from which triketohydrindene hydrate can be isolated by extraction with ether.



This compound is prepared in the same way as alloxantin, namely, by the action of hydrogen sulphide on triketohydrindene hydrate. On passing the gas, at the ordinary temperature, into an aqueous solution of the hydrate, a white precipitate is formed which gradually increases in quantity, and consists of a mixture of hydrindantin and sulphur. After saturation with hydrogen sulphide, the product of the reaction is kept overnight, the solid collected, dried in a vacuum desiccator over sulphuric acid, and then shaken with carbon disulphide. As, by this solvent, the substance cannot be completely freed from sulphur, it must finally be purified by crystallisation. It dissolves in a large quantity of boiling acetone, and separates from the reddish solution in colourless prisms which do not melt, but on heating turn red at 200°, and at 236° decompose completely with evolution of gas.

Hydrindantin, like alloxantin, crystallises with 2 molecules of water, which it loses at 100°.

0.2177* gave 0.4820 CO₂ and 0.0800 H₂O. C = 60.38; H = 4.08.

0.2233, on heating at 100°, lost 0.0228 H₂O. H₂O = 10.21.

C₁₈H₁₀O₆·2H₂O requires C = 60.33; H = 3.91; H₂O = 10.05 per cent.

0.1890† gave 0.4640 CO₂ and 0.0560 H₂O; C = 66.95; H = 3.29.

C₁₈H₁₀O₆ requires C = 67.08; H = 3.10 per cent.

* Air-dried.

† Dried at 100°.

The compound, when dry, is quite stable, but, in solution it readily undergoes a transformation which is indicated by a colour reaction. On boiling it with alcohol, it gradually dissolves to yield a deep reddish violet solution. This change, undoubtedly, is effected by the ammonia which is present in the air of the laboratory, because the same coloration is produced, at once, on treatment of hydrindantin with ammonia. The substance is only very sparingly soluble in boiling water; it dissolves, however, readily in sodium carbonate to form a dark red solution, from which it is precipitated unaltered on the addition of dilute hydrochloric acid, and loses its colour under the influence of oxygen. If sodium hydroxide is used, instead of the carbonate a deep blue solution is produced which, also, loses its colour on passing oxygen into it for a short time, and then contains the salt of *o*-carboxy-mandelic acid. If the colourless alkaline liquor is treated with an excess of dilute sulphuric acid and digested on the water-bath, phthalide-carboxylic acid, $C_6H_4 \begin{array}{c} \text{CH}(\text{CO}_2\text{H}) \\ \text{CO} \end{array} \text{O}$ is produced. This was isolated by extraction with ether and identified by the melting point ($150-151^\circ$) and by analysis. (Found: C=60.49; H=3.39. Calc., C=60.67; H=3.37 per cent.)

With baryta hydrindantin yields a blue precipitate similar to that given with alloxantin, and, like this, loses its colour under the influence of oxygen.

Triketohydrindene Hydrate as a Reagent for Proteins and their Hydrolytic Products.

It was stated before (*loc. cit.*) that triketohydrindene hydrate reacts with amino-acids, dissolved in water, to yield blue solutions. The reaction has since been applied to a considerable number of substances belonging to this class of compounds with the result that not only α -amino-acids but also the corresponding acids with the amino-group in the β -, γ -, δ -, or ϵ -positions respond to the test. Most of these compounds give the colour reaction on slightly warming their aqueous solutions with the reagent, with others, such as β -amino- β -phenylpropionic, α -aminoisobutyric, or α -amino- α -ethylbutyric acids, boiling of the aqueous solutions with the triketone is required. It was pointed out, also, that the reaction depends on the amino-group of the amino-acid being intact; it, therefore, does not occur with phenylglycine or hippuric acid, nor does it take place with proline or hydroxyproline which, instead, give a yellowish-red coloration. Further, it is essential that the carboxyl group of the amino-acid should be intact, for ethyl aminacetate does not respond to the test. This result is of

importance for the interpretation of the chemical reaction which occurs in the production of the blue colour, because it indicates that diketohydrindene hydrate must first be reduced by the amino-acid (and the latter oxidised to the aldehyde) before the colour can be formed. The reduction product, most probably, is hydrindantin, for this readily yields the blue colour reaction with amino-acids. This fact, together with the results of Piloty and Finckh's experiments (*loc. cit.*) on the interaction of alloxan and glycine, throws a light on the constitution of the coloured products. This question will be dealt with in a subsequent paper.

It is of interest to note the difference in the behaviour of triketohydrindene hydrate towards asparagine and glutamine. Whereas the reagent gives with glutamine, as it does with glutamic acid, the characteristic blue coloration, it yields with asparagine a reddish colour reaction as compared with the blue coloration which it forms with aspartic acid. This fact can only be attributed to the difference in the relative positions of the amino-group to the carbamido-group ($\cdot\text{CO}\cdot\text{NH}_2$) in asparagine and glutamine. The polypeptides, like the amino-acids, respond to the test, as, indeed, do the proteins.

Physiological Examination of Triketohydrindene Hydrate.

Since, on account of its sensitive colour-reaction with amino-acids and proteins, triketohydrindene hydrate may prove of use in physiological chemistry, it seemed desirable to have some knowledge of its physiological and toxic properties. Preliminary experiments, kindly carried out at my request in a German laboratory, have shown that the substance is markedly poisonous, the fatal dose for frogs being 0.002—0.005 gram. On hypodermic injection, one of the first symptoms is cardiac paralysis. After injection, triketohydrindene hydrate appears to be readily decomposed. In frogs death may ensue without any of the substance passing into the urine, and the characteristic blue coloration was observed, only, at the site of injection (dorsal lymph sac). The substance is an irritant poison; a solution of 1/1024 per cent. still causes a transitory burning sensation when dropped into the eye. Triketohydrindene hydrate is not, however, a general protoplasmic poison, for the growth of yeast is hardly inhibited; on the second day, the culture had a pronounced blue-violet colour which, however, disappeared on the third day.

In conclusion, I wish to express my best thanks to Professors E. Fischer, Gabriel, Sørensen, and to Dr. Colman, for the large number of

amino-acids and polypeptides they placed at my disposal, which made it possible to apply the reagent in the various directions; I am indebted, also, to Professors Kraemer and Pope for supplying the indene which was required for the preparation of β -hydrindone.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

LXXXV.—*Potassium Cupricarbonates.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

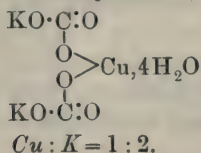
If potassium formed cupricarbonates analogous to all those cupri-compounds which have been isolated, or suggested as existing, in other cases, eight different compounds of copper carbonate with potassium carbonate would exist: these eight compounds have all been isolated, as well as one additional compound. Two are dehydration products of others; one is a gelatinous substance; the other six are crystalline: all have well-marked physical, and, in some cases, chemical properties, differentiating them from each other. In only two cases is the evidence as to composition at all doubtful.

The potassio-cupric carbonate with $4\text{H}_2\text{O}$ (No. 1 below) was first obtained by Deville (*Ann. Chim. Phys.*, 1851, [iii], **33**, 75); it forms hard, fairly large, light blue crystals, resembling many other double copper salts. As it is decomposed by water, it cannot exist as such in the liquid yielding it, and this, it has been suggested (*Trans.*, 1910, **97**, 1838, 1842), contains the β -cupricarbonate, No. 3, the copper in it being present as part of the electronegative ion, although in a very labile condition, for it reacts practically at once with a ferrocyanide. The addition of excess of alkali carbonate to the solution ultimately produces a compound which reacts only very slowly with ferrocyanide, the proportions of carbonate necessary for this change indicating the formation of the compound No. 5 (*loc. cit.*, p. 1830), which would be an α -cupri-compound (that

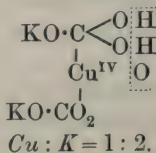
Potassio-cupric Carbonate. β -Cupricarbonate.

No. 1. Tetrahydrate.

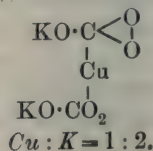
No. 2. Anhydrous.

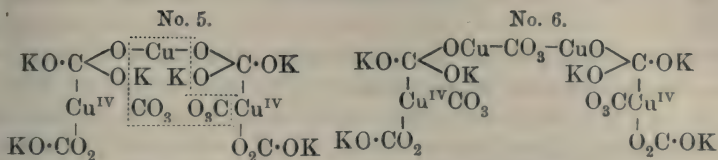
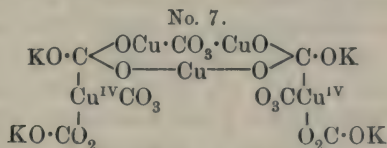
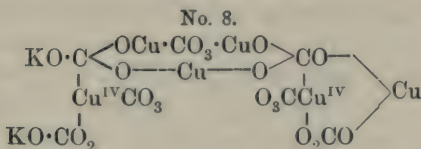
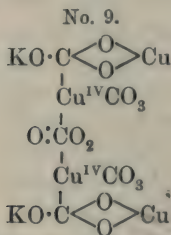


No. 3.



No. 4.



α-Cupricarbonates.

 $\text{Cu} : \text{K} = 3 : 6.$
 $\text{Cu} : \text{K} = 4 : 6.$

 $\text{Cu} : \text{K} = 5 : 4.$

 $\text{Cu} : \text{K} = 6 : 2.$

 $\text{Cu} : \text{K} = 4 : 2.$

is, containing the group $(\text{Cu}^{\text{IV}}\text{CO}_3)''$, of which the analogue in the case of citric acid has been isolated—a compound consisting of two potassio-cupric citrate nuclei united by the elements of $\text{CuK}_2(\text{CO}_3)_2$ (*loc. cit.*, p. 1844). A similar substance has been obtained in the case of the tartrate, except that the double carbonate, in combining with potassium cupritartrate, loses half of its potassium, the compound obtained being analogous to No. 6 (this vol., p. 174). In all the cupri-compounds obtained up to the present, the potassium in the OK groups may, by the action of water or alkali, be easily displaced by copper: such a displacement in this case would give No. 7, then No. 8, and, ultimately, a substance polymeric with normal copper carbonate. In the case of citric acid, a β -cupri-compound derived from three citric acid nuclei was obtained,

$(C_6H_5O_7)_3K_5Cu_2, 2Cu^{IV}O$ (*loc. cit.*, p. 1848), the analogue of which, in the α -cupricarbonates, would be No. 9. No. 4 will be referred to below.

With the exception of the dehydration products, Nos. 2 and 4, these compounds all result directly from the action of copper acetate on potassium carbonate, and, in addition, there are six other products, namely, copper oxide, a basic carbonate, trihydrated potassium carbonate, malachite, potassium acetate, and one unidentified compound, making thirteen products in all, without counting any copper acetate remaining unattacked. The copper oxide and basic carbonate are formed only under exceptional conditions; so, also, is malachite, which can easily be recognised owing to its appearance as small, bright green, hexagonal crystals, adhering strongly to the containing vessel: potassium acetate crystallises only when the liquid is very concentrated, its separation causing the whole liquid to become converted into an opaque, light blue solid.

The action of potassium carbonate solution on solid copper acetate was studied by Reynolds (*Trans.*, 1898, **73**, 262), who found that the resulting liquid deposited, under various conditions which he did not succeed in defining, the double carbonate in the form of (a) large, light blue * crystals of the tetrahydrate, (b) microscopic, blue, silky needles of a monohydrate, and (c) minute, transparent, hexagonal plates of a remarkably strong, deep blue colour, these being anhydrous. Mr. Reynolds has been good enough to present the author with preparations of (a) and (c), and likewise to place his laboratory note-book at his disposal.

It will be shown below that Reynolds was misled as to the composition of the supposed monohydrate, the salt isolated being No. 6, p. 801, which is the main product of the reaction in many cases: and it appeared evident to the author that neither this, nor the deep blue, anhydrous compound, could be mere dehydration products of the tetrahydrate. The tetrahydrate, it is true, does form the anhydrous compound when heated; but it is a change which takes place suddenly at 55° , under circumstances which preclude its being attributable to the mere abstraction of water; for example, when heated in a capillary tube: moreover, the tetrahydrate can be dehydrated in other ways, and then yields a light blue substance.

Similarly, the supposed monohydrate does not give the dark

* Reynolds describes them as greenish-blue: they are quite blue when pure, but look greenish by contrast when still in the mother liquor. Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 174) describe them as "blue, hexagonal crystals," and they, consequently, assume them to consist of a different compound from that obtained by Reynolds: this was evidently not the case, as Wood and Jones' description would apply very closely to the salt prepared by Reynolds.

blue substance on heating, and undergoes no change until it decomposes at about 200° . It has every appearance of being a cupri-compound, as it shows the closest resemblance in the character of its crystallisation to the cupricitrates, etc., whilst the exceptionally dark blue colour of the anhydrous compound indicates that it, also, is probably not an ordinary copper salt.

In order to obtain evidence as to the reaction giving rise to these substances, copper acetate was ground up with various proportions of dissolved potassium carbonate, filtered, and the product examined. The molecular proportions used, where practicable, were:

$\frac{1.}{24}$	$\frac{2.}{12}$	$\frac{3.}{8}$	$\frac{4.}{6}$	$\frac{5.}{4}$	$\frac{6.}{3}$	K to each Cu,
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a normal reaction requiring 4K:Cu. The carbonate solution had specific gravities of 1.55, 1.45 and 1.35 in different series, and with each strength, experiments were made at 10° , 40° and 60° , keeping the mixtures at these higher temperatures for two to three hours before cooling.

The general results, in the light of information subsequently obtained, may be summarised roughly as follows:

Sp. Gr. 1.55. At 10° . With proportion 1, copper oxide separates throughout twenty-four hours; then No. 6. With proportion 5, No. 3 separates at once, and then potassium acetate. Intermediate proportions give mixed products.

At 40° and 60° . Copper oxide separates with the proportions 1 and 2. With higher proportions the results are similar to those at 10° , but the crystallisation is more rapid.

Sp. Gr. 1.45. At 10° . With proportion 1, copper oxide separates throughout three days: no crystallisation. With proportions 2, No. 6 separates, and with proportions 3 and 4, some of No. 1 first, and then some of No. 6. With proportions 3 to 5 there are also increasing amounts of No. 9 formed at once before filtration, and a certain amount of it continues to form in the liquid. With the crystals of No. 1 there are often present dark blue crystals of No. 5.

At 40° and 60° the action is similar, but more oxide is formed with the lower proportions, and, with the higher ones, after cooling, the crystals of the tetrahydrate (No. 1) are interspersed with larger and bluer crystals, which could be picked out, and proved to be the compound $K_2CO_3 \cdot 3H_2O$ coloured with copper.

Sp. Gr. 1.35. At 10° . With proportions 1 and 2, a little basic salt separates, but no crystals: with higher proportions, increasing amounts of No. 1.

At 40° and 60° . Copper oxide separates with the first two

proportions. With the higher proportions, Nos. 7 and 8 separate while the liquid is hot, and, if the heating is prolonged, malachite forms. On cooling, some of No. 1 often separates.

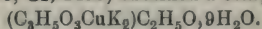
All these substances are decomposed by water, and it is difficult to free them from the mother liquor. Reynolds displaced this by pouring on to them, while on the filter, a mixture of glycerol and alcohol, 1:2 (which does not mix with a saturated solution of potassium carbonate), and then alcohol: this may be fairly satisfactory in the case of large or pulverulent crystals, but in other cases it is not so: experiments with the compound No. 6, with silica, and other substances, showed that the amount of potassium carbonate retained when present as a 1.55 solution might raise the potassium found on analysis by 20 to 30 per cent. and of its proper amount. An error of this magnitude would explain how it was that Reynolds obtained the ratio $\text{Cu}:\text{K}=1:2$ for the substance described by him as the monohydrate, in the place of 1:1.5, as it should have been. He has recently been good enough to reinvestigate the matter, and has been able to confirm the present results, obtaining the ratio 1:1.49.*

If, however, the proportion of glycerol to alcohol is increased to 2:1, the mother liquor dissolves in it, and can be completely removed. As such a mixture is in many cases unfilterable, the method adopted was to incorporate the substance with this mixture, and spread it out in a very thin layer on tiles: when apparently dry, it was mixed with glycerol and alcohol, 1:2, and spread again on tiles: then mixed with glycerol and alcohol, 1:4, put on a filter, and washed with alcohol, being finally dried on a tile or in a vacuum. With two exceptions, none of the substances dealt with were affected by this treatment, although they are all attacked by prolonged treatment with glycerol when moisture is present, some copper passing into solution, and a deliquescent cupriglycerol being formed.†

The various products were also examined by washing them with a little potassium carbonate solution sp. gr. 1.35, the weakest which

* Wood and Jones obtained the same value, 1:2 (details not given), as that originally obtained by Reynolds, when the crystals were filtered off without washing from a mother liquor containing 80 per cent. of potassium carbonate—a sufficient proof that the crystals themselves must have contained less than 2K to each Cu (*loc. cit.*, p. 176).

† Bullnheimer (*Ber.*, 1898, **31**, 1453) obtained a compound



Mr. Reynolds informs the author that he has found washing with glycerol and alcohol, 1:2, to be successful if followed by the use of glycerol, alcohol and water in equal proportions, and then with alcohol.

it is safe to use, and then drying them by working them about on a tile. The carbonate left adhering to them after such treatment is fairly constant with the same substance, but varies with its physical condition: with the potassio-cupric carbonate No. 1, it amounted to 0.9 per cent. of the weight of dried salt; with the finely divided compound No. 6, it was 8 per cent. Such rough analyses afforded a useful check on the results obtained after treatment with glycerol, indicating whether such treatment had altered the substance or not.

The various compounds described below are, except where otherwise stated, fairly stable in air, but after several days' exposure they absorb enough water to become partly converted into a light blue basic salt, probably $5\text{CuO}, 2\text{CO}_2$ (Trans., 1909, **95**, 1412): with excess of water, they all yield this compound, which, on drying, becomes partially converted into malachite. They are all practically dehydrated at 100° , only losing, however, the last traces of water (with a slight loss of carbon dioxide, also) at a higher temperature, but suffer no visible decomposition below 170° to 200° .

No. 1.—Potassio-cupric Carbonate with $4\text{H}_2\text{O}$.—Best prepared by triturating 30 grams of copper acetate with 125 c.c. of potassium carbonate solution sp. gr. 1.45, filtering, and leaving to crystallise. The proportions and strength of carbonate solution may be varied considerably. Any fine, bluish-green deposit of No. 9, which may separate at the same time, can be removed by lixiviation with the mother liquor. Analyses of it confirmed Reynolds' results. It melts at 55° , and forms the deep blue compound, No. 5.

No. 5.—This, however, cannot be prepared quite pure in the above way, as the water cannot be eliminated before it has reacted to form traces of basic salt. The author obtained only a few crystals of it (mixed with other compounds) by the direct action of copper acetate on potassium carbonate, and he is indebted for his knowledge of it to a fine specimen of 30 grams supplied to him by Mr. Reynolds.

The tetrahydrate apparently changes into this compound, even at a lower temperature, for a specimen of the former, which had been kept for twelve years, contained particles of it.

No. 2.—What is apparently the anhydrous potassio-cupric carbonate may be prepared by sprinkling the hydrated salt into a dish of boiling alcohol. It melts, and forms the deep blue compound No. 5: but on grinding it up with the boiling alcohol, it becomes lighter in colour, and, on drying, forms a light blue powder, unaltered at higher temperatures.

No. 6.—Obtained by triturating 10 to 20 grams of copper acetate with 100 c.c. of potassium carbonate solution sp. gr. 1.55, and

filtering so long as any cupric oxide separates. From the stronger solutions it is deposited in what appear to be large crystals, but these consist of sheafs of fine hairs, like bundles of spun glass tied tightly in the middle. From weaker solutions, the crystals are deposited throughout the liquid, giving it a silky sheen, and appearing to fill the whole liquid, but, on filtering under pressure, they are found to occupy only a very small space, forming a thin film on the filter paper, which is easily detached, and itself looks like a piece of blue paper; it can be cut, folded, or torn, the long, silky crystals being knitted together like the cellulose fibres of paper.

After treatment with glycerol and alcohol, and drying at 100°, it gave on analysis: *

	Found.	Calc.
Copper	27.45 = 4.00	27.98 = 4
Potassium	25.22 = 5.98	25.81 = 6

Nos. 7 and 8, as well as the decomposition product (malachite) of what would be the last member of this series, are all formed under nearly similar conditions. When 40 to 60 grams of copper acetate are dissolved in 170 c.c. of potassium carbonate solution sp. gr. 1.35 at temperatures from 60° to 100°, and the product kept at these temperatures for ten to fifteen minutes, a considerable crystallisation occurs, sometimes blue, and sometimes green, more often an evident mixture of the two. The blue crystals are very small, and correspond in composition with No. 7.

	Found.	Calc.
Copper	34.76 = 5.00	34.77 = 5
Potassium	17.89 = 4.07	17.51 = 4

The green crystals are more pulverulent: they were only obtained once without any evident mixtures of No. 7, and then gave:

	Found.	Calc.
Copper	42.43 = 6.00	43.36 = 6
Potassium	10.92 = 2.5	8.89 = 2

indicating that they probably consisted of No. 8, with some of No. 7 mixed with them. They contained no malachite, the crystals of which can be easily recognised under a microscope. Malachite forms only on the prolonged heating of these solutions, appearing as a deposit adhering strongly to the glass.

No. 9 is the compound which separates first whenever copper acetate in sufficient proportion is ground up with potassium carbonate solution of a specific gravity of about 1.45—1.35. The best way to obtain it is to grind 40—60 grams of the acetate with 100 c.c. of

* The mean results from many samples are alone quoted in this and other cases.

the carbonate, pour off the bulk of the liquid, and grind up the undissolved residue afresh: this soon dissolves to form a light blue paste, consisting of a mass of very small crystals, which, after treatment with glycerol and alcohol, and drying at 100° , give:

	Found.	Calc.
Copper	39.55 = 4.00	40.20 = 4
Potassium	12.40 = 2.02	12.36 = 2

No. 3. Potassium β -Cupricarbonate.—To prepare this, 30 grams of copper acetate are triturated with 50 c.c. of potassium carbonate solution sp. gr. 1.55, and filtered under pressure as rapidly as possible. In the filtrate, a gelatinous deposit begins to form, and, as soon as the liquid is thick with it, an equal volume of potassium carbonate solution sp. gr. 1.35 must be added, or it solidifies to an opaque, amorphous mass, interspersed with crystals of potassium acetate. The jelly cannot be actually washed with carbonate solution sp. gr. 1.35 without slight decomposition; also, on treatment with glycerol, unlike all the previously described compounds, it is decomposed, forming a dark violet-blue, sticky mass: its composition, therefore, cannot be exactly determined. After being worked on a tile until apparently dry, and heating at 100° , two samples gave:

	Found.	Corrected.	Calc.
Copper	$\left\{ \begin{array}{l} 20.17 \\ 21.71 \end{array} \right.$	$\left. \begin{array}{l} 21.9 \\ 23.6 \end{array} \right\} = 1.00$	22.72 = 1
Potassium	$\left\{ \begin{array}{l} 29.80 \\ 30.35 \end{array} \right.$	$\left. \begin{array}{l} 27.5 \\ 28.1 \end{array} \right\} = 1.98$	27.95 = 2

The correction applied is based on the assumption that 8 per cent. of potassium carbonate is retained by the salt after being dried in this way (see p. 805). The close concordance between these corrected values and those calculated for the β -cupricarbonate must not be pressed, but, independently of the analyses, it is evident that this substance belongs to a different class from the α -compounds already described.

It appears to be one of the initial products of the action of potassium carbonate and copper acetate, the tetrahydrate and No. 5 being derived from it: thus, if about 60 grams of acetate are dissolved in about 125 c.c. of the carbonate sp. gr. 1.45, and filtered, the filtrate entirely gelatinises after ten minutes, and the dark blue jelly, when collected, or allowed to remain for some time, becomes entirely converted into a mass of light blue tetrahydrate crystals, interspersed with some of the dark blue compound, No. 5, although this latter, in its turn, generally changes into the tetrahydrate also. The metamorphosis of the jelly can be followed under the microscope, and it is brought about instantly by pouring it on to a tile. Interspersed in the jelly there are microscopic,

although relatively large and well formed, elongated, lozenge-shaped crystals of some unidentified compound: these also change into the tetrahydrate.

The metamorphosis of the jelly into the tetrahydrate can be reversed: if the latter is dissolved in strong, cold potassium carbonate solution sp. gr. 1.55, or, preferably, in a still stronger, slightly warmed solution, the deep blue liquid soon gelatinises, and, if strong enough, gradually becomes opaque and almost solid, as in the preparation of No. 3 from the acetate. Such a reaction would by itself be sufficient to show that No. 3 and the tetrahydrate cannot consist of the same substance in different states of hydration. When the liquid is somewhat weaker, the jelly changes, on standing, into a mass of crystals of No. 6.

No. 4.—When tetrahydrated potassio-cupric carbonate (No. 1), in a finely powdered condition, is sprinkled over a sheet of paper and placed on a plate heated to 50° , it darkens, becomes lavender-blue, and loses its water without melting. It does not further change in colour by subsequent heating up to 170° . It is attacked in the same way as the β -cupricarbonate, No. 3, by glycerol, this differentiating it both from No. 2 and the deep blue compound, No. 5, with which it is metameric, suggesting that it is a β -cupricarbonate deprived of the elements of water, that is, No. 4, p. 800. This compound is also obtained by dehydrating the tetrahydrate over sulphuric acid in a vacuum, although it takes some two months to deprive it of all its water.

Unlike the α -cupricarbonates, it is very hygroscopic, forming, on exposure to air, first, a dark blue, sticky mass, which dries up and becomes apparently converted into the tetrahydrate, the latter subsequently forming a basic carbonate, as already described.

Although it is derived from the tetrahydrate under the simplest conditions, and is reconverted into it by hydration, both changes appear to be indirect, and it seems more probable that No. 2, and not this compound, is the anhydrous potassio-cupric carbonate. The difference between this substance and its metamerides, Nos. 2 and 5, was further emphasised by determining their heats of dissolution in dilute hydrochloric acid, the mean results being*:

No. 2.	14462	calories for $(\text{CO}_3)_2\text{CuK}_2$.
No. 4.	12400	„ „
No. 5.	11837	„ „

* Five grams dissolved in 60 c.c. of strong acid diluted to 600 c.c., the specific heat of which was taken as unity, and no allowance made for the heat absorbed by the evolution of carbon dioxide.

General.

The α -cupricarbonates isolated may be represented as consisting of two nuclei of double carbonate with the copper quadrivalent, united by a carbonate group, and the following groups (I, II and III) of such compounds might exist:

α -Cupricarbonates ($R = CO_3$).	β -Cupricarbonates.
I. $a. (R_4K_4Cu^{IV})CuK_2(CO_3)_2$	$a. (R_2K_2Cu^{IV})H_2O$
II. $\left. \begin{array}{l} c. (R_4K_4Cu^{IV})_2Cu_2K_2(CO_3)_3 \\ f. (R_4K_4Cu^{IV})Cu_3(CO_3)_3 \\ g. (R_4K_2CuCu^{IV})Cu_3(CO_3)_3 \\ h. (R_4Cu_2Cu^{IV})Cu_3(CO_3)_3 \end{array} \right\}$	$b. (R_2K_2Cu^{IV})KHO$
III. $i. (R_4K_4Cu^{IV})Cu_4(CO_3)_4$	$c. (R_2K_2Cu^{IV})CuO$
IV. $l. (R_2K_2Cu^{IV})K_2CO_3$	$d. (R_2CuCu^{IV})CuO$
V. $p. (R_3K_2Cu^{IV})Cu_2(CO_3)_2$	

I, a , which is the deep blue compound described above, might give rise to three other members by the substitution of copper for potassium, but these have not been isolated: the individuals in the second group, $e-h$, have all been isolated, except h , of which the decomposition product, malachite, has alone been obtained. The third group of three members (see III, i) is conceivable by substituting a second $-CuCO_3-$ group for the two OK groups in the formula No. 6, p. 801.

So far as the formulæ are concerned, a single double carbonate nucleus (that is, two simple carbonate nuclei) might have a carbonate molecule attached, giving rise to another group, of which IV, l would be the first member, or three simple carbonate nuclei might be similarly united, giving rise to a fifth group, of which V, p would be the third member; this being, apparently, the substance described above as No. 9, p. 801, analogous to one of the β -cupricitrates. More than three carbonate nuclei could not be strung together in this way.

Of the β -cupricarbonates, where oxygen plays the part of CO_3 , the only member probably isolated is a , the action of potassium hydrate being required to produce the others, if they exist. But in the case of the citrates, evidence of the existence of all four members has been given, as well as of another, rendered possible by the acid being tribasic. With the cupritartrates, where $R = C_2H_4O_2CuO$, Nos. a , c , and, probably, d have all been isolated, as well as one consisting of a molecule of a and c united; and c has been isolated in the case of the cuprisaccharate and cuprimucate, as well as in other cases not yet published. It does not seem possible to obtain the member $(R_2K_2Cu^{IV})K_2O$ for reasons previously given (Trans., 1910, 97, 1844).

Just as the nucleus may contain various radicles, so, apparently, may various radicles play the part of the CO_3 in the connecting

group of the α -cupri-salts. By dissolving metallic acetates in potassium succinate solution, Reynolds (Trans., 1898, **73**, 701) obtained a number of double salts, that in the case of copper being represented by the formula $\text{CuK}_4(\text{C}_4\text{H}_4\text{O}_4)_3$, and being inexplicable on the then existing views, except as a "molecular" compound: but it may now be represented as the analogue of the α -cupricarbonate IV, *l*, above, and it forms blue, microscopic crystals with a slight violet tinge, suggestive of its being a cupri-compound. The present author has obtained the ordinary potassio-cupric salt, $\text{CuK}_2(\text{C}_4\text{H}_4\text{O}_4)_2$, which forms large, hard crystals of a pure blue colour, and which, unlike Reynolds' salt, is not decomposed by water, unless the solution is dilute (0.17 per cent. Cu).

The same method was applied by the author to obtain indications as to which acids probably form cupri-salts under like conditions. In the following cases, deeply coloured, viscous liquids were obtained, from which minute, soft crystals gradually separated, or from which no crystals were obtained, but cupri-compounds were precipitated by alcohol: lactate, malate (two forms of crystals), glycollate (two forms of crystals, one of which gave $(\text{C}_2\text{H}_3\text{O}_3)_7\text{Cu}_4\text{K}$ on analysis), glycerate (giving $(\text{C}_3\text{H}_5\text{O}_4)_4\text{K}(\text{CuO})_4$), tartrate (Cu:K about 3:1), quinate (giving $(\text{C}_7\text{H}_{11}\text{O}_6)_2\text{Cu}, 3\text{CuO}$, and also an ordinary basic salt, $(\text{C}_7\text{H}_{11}\text{O}_6)_2\text{Cu}, \text{CuO}$), and citrate (giving $(\text{C}_6\text{H}_5\text{O}_7)_2\text{K}_2\text{Cu}_2, \text{CuO}$, previously obtained in other ways, Trans., 1910, **97**, 1846).

On the other hand, limpid solutions of what appeared to be ordinary cupric salts were obtained with the fumarate, aconitate (including an acid salt, $\text{C}_6\text{H}_3\text{O}_6\text{CuH}$), salicylate, mucate, phthalate (the double salt, $(\text{C}_8\text{H}_4\text{O}_4)_2\text{CuK}_2$, and a basic copper salt with 2 or 3 CuO being obtained), toluate, protocatechuate (the double salt $(\text{C}_5\text{H}_6\text{O}_4)_3\text{Cu}_2\text{K}_2$ being obtained), pyrotartrate, and malate (giving $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Cu}_2\text{K}_2$ *).

With the benzoate, oxalate and cinnamate, no action at all took place.

None of the compounds above mentioned, except the citrate, appear to have been previously obtained.

There does not seem to be any evident connexion between the constitution of the acid and the nature of the reaction in such cases: all the acids forming cupri-compounds contain alcoholic hydroxyl, but the presence of such hydroxyl does not necessarily involve the formation of cupri-compounds.

The last member of each of the five series of α -cupricarbonates would be a polymeride of normal copper carbonate, and, like it, would probably be incapable of a separate existence: but other

* The liquid was viscid in this case, but the crystals were gritty, like those of an ordinary cupric salt,

copper salts are not so unstable, and it is possible that in their case they might exist as ordinary cupric salts, and also as copper cupri-salts.

There is only one instance where members of the series shown above would be polymeric, *b* and *m*, neither of which have been isolated, but *a* (No. 5 on p. 801) is polymeric with anhydrous potassio-cupric carbonate (No. 2, p. 800), and also with the dehydrated β -cupricarbonate (No. 4, p. 800), and it has been shown that these three compounds are well characterised by differences in physical and chemical properties. This is of special interest in view of the fact that the author established twenty-five years ago (Trans., 1886, **49**, 1) that anhydrous potassio-cupric sulphate exists in three distinct modifications, well differentiated by their colour and heats of dissolution, and of this no explanation has been forthcoming until now.

HARPENDEN,
HERTS.

LXXXVI.—*The Absorption Spectra of Chlorobenzene and Bromobenzene as Vapours, as Liquids, and in Solution.*

By JOHN EDWARD PURVIS.

THE author has already given accounts of the absorption spectra of various compounds under different physical conditions (Trans., 1910, **97**, 692, 1035, 1649, 1546). The conclusions drawn from those observations were that the physical conditions affect the absorption of light very markedly, and that whilst the vapours of some of the substances showed a considerable number of bands, their allied and homologous compounds showed either fewer or none at all. Moreover, the solutions of the substances proved that the absorption was again considerably altered, and that there were fewer bands and of a different type: also that very thin films of such substances showed no selective absorption at all.

The investigation has been continued with chlorobenzene and bromobenzene; and the aim of the experiments was to ascertain (1) the nature of the absorption of the radiant energy, and (2) how far the displacement of one atom of hydrogen by chlorine or bromine affects the type of absorption, when the vapours were under various conditions of temperature and pressure, when they were in solution in alcohol, and when they were in very thin films.

The substances were obtained from Kahlbaum, and were re-distilled at constant boiling point; the apparatus employed has been described before (*loc. cit.*).

Vapours.—Chlorobenzene.

TABLE I.

The absorption spectrum of the vapour of chlorobenzene in a 1-dcm. tube has been studied by Pauer (*Wied. Ann.*, 1897, **61**, 363), who observed fifteen bands at 35°.

The absorption bands in chlorobenzene vapour at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter are as follows:

Abbreviations: f.str.=fairly strong; str.=strong; w.=weak; v.w.=very weak; narr.=narrow; m.w.=moderately weak; m.str.=moderately strong; v.narr.=very narrow.

	15°. 749 mm. λ.	30°. 793 mm. λ.	45°. 819 mm. λ.
I.	2746 f.str.	2746 f.str.	2746 f.str.
	2721 w.	2721 w.	2721 w.
	2720 w.	2720 w.	2720 w.
	2719 w.	2719 w.	2719 w.
	2717 w.	2717 w.	2717 w.
	2715 str.	2715 str.	2715 str.
	2712 m.str.	2712 m.str.	2712 m. str.
	2710 m.w.	2710 m.w.	2710 m.w.
	2708 m.w.	2708 m.w.	2708 m.w.
	2706 w., narr.	2706 w., narr.	2706 w., narr.
II.	2703 str.	2703 str.	2703 str.
	2701 v.narr., w.	2701 v.narr., w.	2701 v.narr., w.
	2698 str.	2698 str.	2698 str.
	2684 v.w.	2684 v.w.	2684 v.w.
	2682 v.w.	2682 v.w.	2682 v.w.
	2681 v.w.	2681 v.w.	2681 v.w.
	2678 v.w.	2678 v.w.	2678 v.w.
	2674 f.str.	2674 f.str.	2674 f.str.
	2673 v.w., narr.	2673 v.w., narr.	2673 v.w., narr.
	2672 f.str.	2672 f.str.	2672 f.str.
III.	2669 f.str.	2669 f.str.	2669 f.str.
	2667 w., narr.	2667 w., narr.	2667 w., narr.
	2664 str.	2664 str.	2664 str.
	2663 v.w., narr.	2663 v.w., narr.	2663 v.w., narr.
	2661 str.	2661 str.	2661 str.
	2655 v.w., narr.	2655 v.w., narr.	No rays transmitted beyond 2660, but the Cd. lines 2573 to 2267 were visible.
	2653 v.w.	2653 v.w.	
	2652 w.	2652 w.	
	2650 w.	2650 w.	
	2648 w.	2648 w.	
	2646 w.	2646 w.	
	2643 w., wide	2643 w., wide	
	2642 w., narr.	2642 m.narr.	
	2638 m.w.	2638 m.w.	
	2636 m.w.	2636 m.w.	
	2634 m.w.	2634 m.w.	25 bands.
	2632 m.w.	2632 m.w.	
	2630 w.	2630 w.	
	2629 w.	2629 w.	
	2626 w., narr.	2626 w., narr.	
	2624 f.str.	2624 f.str.	
	2622 f.str.	2622 f.str.	

TABLE I (*continued*).

15°.	30°.	60°.
749 mm.	793 mm.	849 mm.
λ.	λ.	λ.
IV. { 2621 f.str. 2619 w. 2617 w. 2615 w. 2612 w. 2610 w. 2607 f.str. 2605 v.w. 2603 w. 2600 f.str. 2599 f.str. 2597 v.w., narr. 2595 f.str. 2594 f.str. 2591 w. 2588 w. 2586 w. 2571 w. 2569 w. 2566 w. 2564 w. 2562 w. 2560 w. 2557 w. 2555 w. 2538 v.w. 2536 v.w. 2533 v.w. 2526 v.w. 2495 v.w.	IV. { 2621 f.str. 2619 w. 2617 w. 2615 w. 2612 w. 2610 w. 2607 f.str. 2605 v.w. 2603 w. 2600 f.str. 2599 f.str. 2597 v.w., narr. 2595 f.str. 2594 f.str. 2591 w. 2588 w. 2586 w. 2571 w. 2569 v.w. 2566 v.w. 2564 v.w. 2557 v.w. 2554 v.w.	I. { 2745 f.str. 2721 w. 2720 w. 2719 w. 2717 w. 2714 f.str. 2712 m.str. 2710 m.str. 2708 m.str. 2706 w., narr. 2704 f.str. 2701 v.w. 2698 f.str.
	Rays absorbed from 2500, but the Cd. lines 2329 to 2267 were visible.	Rays absorbed from 2690, but the Cd. lines 2573 to 2267 were just visible.
	67 bands.	13 bands.
		75°.
		879 mm.
		2746 f.str.
		All rays absorbed from 2720; the Cd. lines 2573 to 2267 were just visible.
		1 band.
		90°.
		909 mm.
		2746 str.
		All rays absorbed from 2735; the Cd. lines 2573 to 2267 were very weak.
		1 band.
		100°.
		925 mm.
		2746 str.
		All rays absorbed from 2740; the Cd. lines 2573 to 2267 were just visible.
		1 band.

The strong Cd. lines 2473, 2329, 2321, 2313, 2306, 2288, 2267, 2239 were visible.
72 bands.

Chlorobenzene.

TABLE II.

The absorption bands in chlorobenzene vapour at a constant temperature of 15° and at various pressures. Abbreviations as in table I.

742 mm. λ.	512 mm. λ.	442 mm. λ.	312 mm. λ.	162 mm. λ.	12 mm. λ.
2746 f.str. 2721 w. 2720 w. { 2719 w. 2717 w. 2714 str. 2712 m.w. { 2710 m.w. 2708 m.w. 2705 w., narr. 2703 str. 2702 v.w., narr. 2698 str. 2684 v.w. 2682 v.w. 2681 v.w. 2678 v.w. 2674 f.str. 2673 v.w., narr. { 2672 f.str. 2669 f.str. 2667 w., narr. 2665 str. 2663 v.w., nar.. 2661 str.	<p>The bands at this pressure were similar to those observed at 742 mm., except that they were slightly sharper and clearer. The Cd. lines 2329 to 2239 were well marked.</p> <p>It should also be noted that the series of four absorption bands from 2638 to 2632, and also the series of six bands from 2615 to 2604 were much clearer and sharper than at 742 mm.</p>	<p>The bands at this pressure were very like those at 512 mm., except that they were sharper and weaker.</p>	<p>The bands at this pressure were like those observed at 442 mm., except that they were much weaker and also sharper. The Cd. lines from 2473 to 2239 were well marked.</p>	<p>I. { 2714 f.str. 2712 w. 2710 w. 2705 w. 2703 f.str. 2702 v.w. 2698 f.str.</p> <p>I. { 2714 v.w. 2703 v.w. 2698 v.w.</p>	<p>I. { 2674 v.w. 2672 v.w. 2669 v.w. 2665 v.w. 2661 v.w.</p> <p>II. { 2674 v.w. 2672 v.w. 2669 v.w. 2665 v.w. 2661 v.w.</p>

TABLE II (*continued*).

	742 mm. λ.	162 mm. λ.	12 mm. λ.		
	2655 v.w., narr.				
III.	{ 2653 v.w.				
	{ 2652 w.				
	{ 2650 w.				
	{ 2647 w.				
	{ 2645 w.				
	2643 w., wide				
	2642 w., narr.				
	{ 2638 v.w.	III. {	{ 2638 w.		
	{ 2636 v.w.		{ 2636 w.		
	{ 2634 v.w.		{ 2634 w.		
	{ 2632 v.w.		{ 2632 w.		
2630 w.					
2629 w.					
2626 w., narr.					
2624 f.str.	{ 2624 f.str.	2624 v.w.			
2622 f.str.		{ 2622 f.str.	{ 2622 v.w.		
2621 f.str.	2621 f.str.	2621 w.			
IV.	{ 2620 w.	IV. {	IV. {		
	{ 2617 w.				
	{ 2615 w.				
	{ 2612 w.				
	{ 2610 w.	IV. {	IV. {		
	{ 2608 f.str.				
	{ 2606 v.w.				
	{ 2604 w.				
	2601 f.str.			2608 f.str.	2607 v.w.
	2599 f.str.			2601 f.str.	2602 v.w.
	2597 w., narr.			2599 f.str.	2599 v.w.
	{ 2595 f.str.			2525 f.str.	2594 v.w.
	{ 2593 f.str.	2593 f.str.	2593 v.w.		
	2591 w.				
	{ 2588 w.				
	{ 2586 w.				
	2574 w.				
	{ 2572 w.				
	{ 2570 m.w.	{ 2570 w.	{ 2570 v.w.		
	{ 2567 m.w.			{ 2567 w.	{ 2567 v.w.
{ 2564 m.w.	{ 2564 w.			{ 2564 v.w.	
{ 2562 w.	2562 w.			2562 v.w.	
{ 2559 w.					
{ 2557 w.					
{ 2555 w.					
{ 2538 v.w.	No bands were visible beyond 2562, but the Cd. lines to 2194 were well marked.				
{ 2536 v.w.					
{ 2533 v.w.					
{ 2526 v.w.	No bands were beyond this; the Cd. lines to 2194 were well marked.				
2495 v.w.					
	31 bands.	24 bands.			

The Cd. lines 2473 to 2239 beyond this were well marked.

73 bands.

Bromobenzene.

TABLE III.

The absorption spectrum of the vapour of bromobenzene in a 1-dm. tube has been studied by Pauer (*loc. cit.*), who observed fourteen bands at 35°.

The absorption bands in bromobenzene vapour at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter are as follows. Abbreviations as before.

17°.	30°.	45°.	60°.	75°.	90°.	100°.
λ.	λ.	λ.	λ.	λ.	λ.	λ.
757 mm.	801 mm.	827 mm.	857 mm.	887 mm.	917 mm.	933 mm.
2759 v.w.		2761 v.w.	2760 v.w.	2761 v.w.	2671 v.w.	2761 v.w.
2728 w.	Similar bands to those at 17° and 757 mm. were observed, except that they were slightly stronger.	2760 w.	2759 w.	2759 w.	2759 w.	2759 f.str.
2722 w.		2728 w.	2729 w.			
2720 f.str.		2722 w.	2728 w.	2728 widens into 2729	2728 w., wide	2728 w., wide
		2719 f.str.	2720 f.str.	2720 f.str., widens into 2722	2720 w., wide	2720 w., wide
				2718		
2718 w.		2718 w.	2718 w.			
2716 w.		2716 w.	2716 w.			
2715 f.str.		2715 f.str.	2715 f.str.			
2713 w., narr.		2713 w., narr.	2712 w., narr.	2715 f.str., widens into 2716	2715 w., wide	2715 w., wide
2712 v.w., narr.		2712 str.	2711 str.	2711 f.str., widens into 2712 & 2710	2711 w., wide	2711 w., wide
2711 str.						
2710 w., narr.		2710 w., narr.	2710 w., narr.			
2707 str.		2707 str.	2707 str.	2707 str.	2707 w., wide	2707 w., wide

TABLE III (continued).

17° λ.	30° λ.	45° λ.	60° λ.	75° λ.	90° λ.	100° λ.	
2702 v.w. 2699 v.w. 2695 v.w. 2689 f.str. 2686 f.str. 2681 v.w. 2676 v.w. 2675 v.w., narr. 2672 str. 2671 w., narr. 2666 str. 2665 v.w. 2663 v.w. 2662 v.w. 2660 w. 2657 w. 2655 w. 2652 w. 2647 v.w. 2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str.	The rays then transmitted to Cd. 2329, and the series of Cd. lines to 2288 well marked. 62 bands.	2702 v.w. 2699 v.w. 2695 v.w. 2690 f.str. 2686 f.str. 2682 v.w. 2676 v.w. 2675 v.w. 2673 str. 2671 w., narr. 2667 str. 2664 v.w. 2663 v.w. 2662 v.w. 2659 w. 2656 w. 2654 w. 2652 w. 2647 w. 2646 f.str. 2644 f.str. 2640 f.str. 2639 f.str. 2637 w. 2635 f.str.	857 mm. 2702 v.w. 2699 v.w. 2695 v.w. 2689 f.str. 2686 f.str. 2681 v.w. 2676 v.w. 2675 v.w. 2672 str. 2671 w. 2666 str. 2665 v.w. 2663 v.w. 2662 v.w. 2660 w. 2657 w. 2655 w. 2652 w. 2647 w. 2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str.	887 mm. 2689 f.str. 2686 f.str. 2676, widens } into 2675 } 2672, widens } into 2671 } 2666 str.	917 mm. 2689 f.str. 2686 f.str. 2676 w. 2672 f.str. 2666 f.str.	938 mm. Rays transmitted to about 2690, the Cd. 2573 being well marked. 7 bands.	
I.		II.	II.	II.	II.		
I.		III.	III.	III.			
				2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. These last four bands almost infringe on one another. 2635 f.str., widens } into 2637 }			

17°	45°	60°	75°
757 mm.	827 mm.	857 mm.	887 mm.
λ .	λ .	λ .	λ .
<div>IV.</div> <div> { 2633 v.w., nart. 2630 v.w. 2628 v.w. 2626 v.w. 2624 v.w. 2622 v.w. 2620 v.w. 2612 v.w. 2608 w. 2604 str. 2602 str. 2601 v.w., nart. 2598 f.str. 2592 w. 2572 f.str. 2570 f.str. 2567 f.str. 2565 f.str. 2545 w. 2538 v.w. 2535 v.w. 2534 v.w. 2512 v.w. 2500 v.w. 2488 v.w. </div>	<div>IV.</div> <div> { 2633 v.w. 2630 v.w. 2628 v.w. 2627 v.w. 2624 v.w. 2621 v.w. 2620 v.w. 2612 v.w. 2607 v.w. 2604 str. 2601 str. 2601 v.w. 2597 f.str. 2592 v.w. 2572 f.str. 2570 f.str. 2568 f.str. 2566 f.str. 2545 v.w. 2536 v.w. </div>	<div>IV.</div> <div> { 2633 v.w. 2630 v.w. 2628 v.w. 2626 v.w. 2624 v.w. 2622 v.w. 2620 v.w. 2612 v.w. 2608 v.w. 2604 w. 2602 w. 2601 v.w. 2598 w. 2592 w. 2572 w. 2570 w. 2567 w. 2565 w. </div>	<div>IV.</div> <div> { 2504 2597 </div>
<p>Rays transmitted to Cd. lines to 2265 well marked.</p> <p>62 bands.</p>	<p>Rays transmitted to about 2400, and the three Cd. lines 2329, 2321, 2313 just visible.</p> <p>58 bands.</p> <p>The bands were a little wider than at 17° and 30°.</p>	<p>Rays transmitted to about 2420, the Cd. lines 2313 and 2321 just visible.</p> <p>56 bands.</p>	<p>Rays transmitted to about 2490.</p> <p>20 bands.</p> <p>The bands were wider than at the lower temperatures and pressures.</p>

Bromobenzene.

TABLE IV.

The absorption bands in bromobenzene vapour at a constant temperature of 15° and at various pressures.
Abbreviations as before.

722 mm. λ.	642 mm. λ.	342 mm. λ.	192 mm. λ.	47 mm. λ.
I. { 2729 w. 2728 w. 2722 w. 2720 f.str. 2718 w. 2716 w. 2715 f.str. 2712 v.w., narr. 2711 str. 2710 w., narr. 2707 str.	I. { 2720 f.str. 2715 f.str. 2712 v.w. 2711 str. 2710 2707 str.	I. { 2720 f.str. 2715 f.str. 2711 f.str. 2707 f.str.	I. { 2720 w. 2715 w. 2711 w. 2706 w.	I. { 2720 v.w. 2715 v.w. 2711 v.w. 2706 v.w.
II. { 2689 f.str. 2686 f.str. 2681 f.str. 2675 v.w. 2672 str. 2671 w., narr. 2666 str.	II. { 2689 f.str. 2686 f.str. 2681 f.str. 2675 v.w. 2672 str. 2671 v.w. 2666 str.	II. { 2689 f.str. 2686 f.str. 2672 f.str. 2666 str.	II. { 2689 w. 2686 w. 2672 w. 2666 w.	II. { 2689 w. 2686 w. 2672 w. 2666 w.

<p>0.12 mm. λ.</p> <p>2665 v.w. 2663 v.w. 2662 v.w. 2660 w. 2657 w. 2655 w. 2652 w. 2647 v.w. 2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str. 2633 v.w., narr. 2630 v.w. 2628 v.w. 2626 v.w. 2624 v.w. 2622 v.w. 2620 v.w. 2612 v.w. 2608 w. 2604 str. 2602 str. 2601 v.w., narr. 2598 f.str. 2592 w. 2572 w. 2570 w. 2567 w. 2565 w.</p> <p>III.</p>	<p>2660 w.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2635 w.</p> <p>IV.</p> <p>2604 str. 2602 str. 2598 f.str.</p> <p>IV.</p> <p>2572 v.w. 2570 v.w. 2567 v.w. 2565 v.w.</p>	<p>2645 v.w. 2643 v.w. 2640 v.w. 2638 v.w. 2635 v.w.</p> <p>III.</p>	<p>The rays were trans- mitted to 2350, and the Cd. lines 2329 to 2265 were well marked.</p>	<p>The rays were trans- mitted to Cd. 2265.</p>	<p>13 bands.</p>	<p>12 bands.</p>
<p>0.12 mm. λ.</p> <p>2665 v.w. 2663 v.w. 2662 v.w. 2660 w. 2657 w. 2655 w. 2652 w. 2647 v.w. 2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str. 2633 v.w., narr. 2630 v.w. 2628 v.w. 2626 v.w. 2624 v.w. 2622 v.w. 2620 v.w. 2612 v.w. 2608 w. 2604 str. 2602 str. 2601 v.w., narr. 2598 f.str. 2592 w. 2572 w. 2570 w. 2567 w. 2565 w.</p> <p>III.</p>	<p>2660 w.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2635 w.</p> <p>IV.</p> <p>2604 str. 2602 str. 2598 f.str.</p> <p>IV.</p> <p>2572 v.w. 2570 v.w. 2567 v.w. 2565 v.w.</p>	<p>2645 v.w. 2643 v.w. 2640 v.w. 2638 v.w. 2635 v.w.</p> <p>III.</p>	<p>The rays were trans- mitted to 2350, and the Cd. lines 2329 to 2265 were well marked.</p>	<p>The rays were trans- mitted to Cd. 2265.</p>	<p>13 bands.</p>	<p>12 bands.</p>
<p>0.12 mm. λ.</p> <p>2665 v.w. 2663 v.w. 2662 v.w. 2660 w. 2657 w. 2655 w. 2652 w. 2647 v.w. 2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str. 2633 v.w., narr. 2630 v.w. 2628 v.w. 2626 v.w. 2624 v.w. 2622 v.w. 2620 v.w. 2612 v.w. 2608 w. 2604 str. 2602 str. 2601 v.w., narr. 2598 f.str. 2592 w. 2572 w. 2570 w. 2567 w. 2565 w.</p> <p>III.</p>	<p>2660 w.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2635 w.</p> <p>IV.</p> <p>2604 str. 2602 str. 2598 f.str.</p> <p>IV.</p> <p>2572 v.w. 2570 v.w. 2567 v.w. 2565 v.w.</p>	<p>2645 v.w. 2643 v.w. 2640 v.w. 2638 v.w. 2635 v.w.</p> <p>III.</p>	<p>The rays were trans- mitted to 2350, and the Cd. lines 2329 to 2265 were well marked.</p>	<p>The rays were trans- mitted to Cd. 2265.</p>	<p>13 bands.</p>	<p>12 bands.</p>
<p>0.12 mm. λ.</p> <p>2665 v.w. 2663 v.w. 2662 v.w. 2660 w. 2657 w. 2655 w. 2652 w. 2647 v.w. 2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str. 2633 v.w., narr. 2630 v.w. 2628 v.w. 2626 v.w. 2624 v.w. 2622 v.w. 2620 v.w. 2612 v.w. 2608 w. 2604 str. 2602 str. 2601 v.w., narr. 2598 f.str. 2592 w. 2572 w. 2570 w. 2567 w. 2565 w.</p> <p>III.</p>	<p>2660 w.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2635 w.</p> <p>IV.</p> <p>2604 str. 2602 str. 2598 f.str.</p> <p>IV.</p> <p>2572 v.w. 2570 v.w. 2567 v.w. 2565 v.w.</p>	<p>2645 v.w. 2643 v.w. 2640 v.w. 2638 v.w. 2635 v.w.</p> <p>III.</p>	<p>The rays were trans- mitted to 2350, and the Cd. lines 2329 to 2265 were well marked.</p>	<p>The rays were trans- mitted to Cd. 2265.</p>	<p>13 bands.</p>	<p>12 bands.</p>
<p>0.12 mm. λ.</p> <p>2665 v.w. 2663 v.w. 2662 v.w. 2660 w. 2657 w. 2655 w. 2652 w. 2647 v.w. 2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str. 2633 v.w., narr. 2630 v.w. 2628 v.w. 2626 v.w. 2624 v.w. 2622 v.w. 2620 v.w. 2612 v.w. 2608 w. 2604 str. 2602 str. 2601 v.w., narr. 2598 f.str. 2592 w. 2572 w. 2570 w. 2567 w. 2565 w.</p> <p>III.</p>	<p>2660 w.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2637 w., narr. 2635 str.</p> <p>III.</p> <p>2645 f.str. 2643 f.str. 2640 f.str. 2638 f.str. 2635 w.</p> <p>IV.</p> <p>2604 str. 2602 str. 2598 f.str.</p> <p>IV.</p> <p>2572 v.w. 2570 v.w. 2567 v.w. 2565 v.w.</p>	<p>2645 v.w. 2643 v.w. 2640 v.w. 2638 v.w. 2635 v.w.</p> <p>III.</p>	<p>The rays were trans- mitted to 2350, and the Cd. lines 2329 to 2265 were well marked.</p>	<p>The rays were trans- mitted to Cd. 2265.</p>	<p>13 bands.</p>	<p>12 bands.</p>

The rays were trans-
mitted to about 2400,
and the series of Cd.
lines 2329 to 2265 were
visible.

16 bands
and they were sharper
than at 642 mm.

The rays were trans-
mitted to about 2480,
and the Cd. lines 2329
to 2265 were visible.

20 bands
and they were a little
sharper than at 772 mm.

The rays were trans-
mitted to about 2400,
and the Cd. lines 2329
to 2265 were visible.

54 bands.

However, there are several individual members of the groups which are very similar in appearance, as, for example:

Group.	Chlorobenzene. λ.	Bromobenzene. λ.
I.	2698	2707
	2701	2710
	2703	2711
II.	2661	2666
	2663	2671
	2664	2672
III.	2640	2645
	2638	2643
	2635	2640
	2633	2638
IV.	2598	2604
	2596	2602
	2571	2572
And also the group of bands.	2569	2570
	2566	2567
	2564	2565

It should be stated that each band was separately measured at the different temperatures and pressures, and on the more refrangible edges. The bands are more of the nature of strong lines than of what is usually understood by a band, and in this respect they are very like those which were observed by the author in the vapours of pyridine, aniline, etc. (*loc. cit.*). The width of some of these bands is not a measurable one, and in constitution and appearance they are different from those observed in the vapours of benzene by Hartley (*Phil. Trans.*, 1908, A, **208**, 475).

General Results of the Absorption Spectra of the Vapours.

The results of the preceding observations of the vapours of chlorobenzene and bromobenzene indicate that (1) both vapours possess a considerable number of absorption bands, which show general relationships amongst themselves, both in structure and in differences of wave-lengths. (2) Each vapour has four principal groups which are comparable in their general appearance, and some of the individual members of corresponding groups have a very similar appearance. (3) The groups of bands of bromobenzene are shifted more towards the red end of the spectrum than the corresponding groups of the chlorobenzene vapour. (4) An increase in the temperature and pressure causes a slight widening of the bands, and the general absorption is shifted towards the less refrangible regions of the spectrum; and (5) under decreased pressure, the bands become sharper and wider, and the general absorption is shifted towards the more refrangible regions.

Solutions in Alcohol.

Baly and Collie (Trans., 1905, **87**, 1332) have described the absorption curves of chlorobenzene. Since then, Baly has made some corrections (Proc., 1911, **27**, 72); and the author has made observations of the absorption spectra of chlorobenzene which confirm the later results. These results prove that alcoholic solutions show seven bands which are unlike the vapour bands. Moreover, equimolecular solutions of bromobenzene in alcohol were examined, and seven bands were also observed. The positions of the heads of these bands were as follows:

<i>M</i> /100-Chlorobenzene.	<i>M</i> /100-Bromobenzene
λ .	λ .
2714 f.str.	2718 f.str.
2645 str.	2649 str.
2622 „	2617 „
2577 f.str.	2581 f.str.
2549 str.	2553 str.
2510 w.	2515 v.w.
2450 v.w.	2455 v.w.

Besides the differences in the positions of the bands, the general absorption on the more refrangible side of the bromobenzene solution was shifted more towards the less refrangible regions as compared with similar strengths and thicknesses of the chlorobenzene solution. For example:

M/100-chlorobenzene at 2 mm. thickness: general absorption began at λ 2260.

M/100-bromobenzene at 2 mm. thickness: general absorption began at λ 2400.

The solution bands are completely different from those of the vapours. The former are wider and diffuse, and they are slightly more diffuse on the less refrangible than on the more refrangible edges; whereas the vapour bands are narrower and many in number, as described in the preceding pages.

Liquids in Thin Films.

Very thin films of chloro- and bromo-benzene were also examined. This was accomplished by gently pressing a drop of the liquid between two quartz plates centred in front of the slit of the spectro-scope, and the rays from a condensed cadmium spark were passed through for five minutes. Seven bands were observed, and the following numbers are the heads of the bands of the two substances:

Chlorobenzene.	Bromobenzene.
λ .	λ .
2722 f.str.	2725 f.str.
2651 "	2654 "
2619 "	2621 mod. weak.
2583 "	2585 "
2556 v.w.	2558 "
2516 f.str.	2518 w.
2467 v.w.	2470 v.w.
The rays were then feebly transmitted to about λ 2305.	The rays were then feebly transmitted to about λ 2435.

The bands are very similar in appearance to those observed in the alcoholic solutions: they are wide and diffuse, and more diffuse on the less than on the more refrangible edges.

General Results and Conclusions.

The principal results of the preceding observations are: (1) that the vapours of chlorobenzene and of bromobenzene exhibit a considerable number of narrow bands which can be divided into four chief, well-defined groups, besides several minor groups, and the positions of these groups are shifted more towards the red end of the spectrum in the bromobenzene vapour; that there are variations in the intensities in the constituent members of the groups, particularly of the four well-defined groups; and that the bands as a whole can be arranged in series showing fairly regular differences in their wave-lengths. (2) Alcoholic solutions of the two substances of equimolecular strengths, through equal thicknesses, exhibit seven wide diffuse bands which are comparable in appearance, and are shifted more towards the less refrangible end of the spectrum in the bromobenzene solution. (3) Very thin films of the two substances exhibit seven wide diffuse bands which are comparable in appearance, and they are also comparable with the solution bands; but they are shifted more towards the less refrangible regions, and the bands of the bromobenzene film are shifted more towards the less refrangible regions than those of the chlorobenzene film.

Hartley (*Phil. Trans.*, 1908, A, 208, 475) has examined the absorption spectra of the vapours of benzene and its homologues, and of solutions of benzene; and he compares the benzene solution which shows seven bands with the vapour which exhibits eighty-four bands at 25° and 759.5 mm. The author has taken photographs of the absorption of the vapours of benzene, toluene, and aniline under the conditions of temperature and pressure similar to those applied to the vapours of chloro- and bromo-benzene, but no coincidence was observed in the respective bands. The only general similarity was that the most refrangible constituents of the groups were the strongest, and then the constituents shaded off in intensity on the

less refrangible sides. The introduction of one atom of chlorine or of bromine in the place of hydrogen or methyl or NH_2 , alters the extent of the absorption with regard to position, and also the type of absorption is considerably changed. Moreover, the substitution diminishes the total number of bands; for the maximum number of bands found by Hartley in benzene vapours was 84, and the maximum number of bands is 72 in the vapour of chlorobenzene, and 62 in the vapour of bromobenzene. The diminution in the number of vapour bands is analogous to the diminution observed by Hartley when the hydrogen atoms of benzene are replaced by methyl or ethyl groups (*loc. cit.*).

In the alcoholic solutions and in the thin films of chlorobenzene and bromobenzene, the vibrations of the ring are such as to show that the selective absorptions are closely comparable; the chief difference is in the relative positions of the bands, and these are controlled by the relative weights of the vibrating molecules.

The vapour molecules have a greater freedom of movement, and the number of encounters producing oscillations or vibrations in a given time depends on this freedom. The result is apparent in a considerable number of bands, the type of which is conditioned largely by the nature of the substituting atoms; but neither chlorine nor bromine, when substituting each other in the benzene molecule, produces a very great difference in the type of absorption, a result which might be expected from other considerations of the influence of the halogen atoms. The chief differences are variations in the intensities and relative positions of the various groups; whereas, as a whole, the groups are very similar, and they differ in position as a consequence of the heavier bromine atom.

The movements of the molecules in solution are considerably restricted; for the solvent not only exerts a restraining effect on the vibrations or oscillations, but it acts as a barrier to the number of encounters, and also as an absorbent of a portion of the radiant energy. The effect is apparent in the different type of selective absorption. In the thin films, the movements of the molecules are also restricted, as a consequence of the tensional effect resulting from a closer packing. The selective absorption, however, is similar to that of the solutions, indicating that the oscillations are not unlike. The chief difference is that the bands are shifted more towards the less refrangible region, and the difference may be caused by the more closely packed molecules of the films interfering with the rate of vibration.

The results of a comparative study and a more complete discussion of the absorption spectra of the *o*- and *m*-dichloro- and dibromo-

benzenes, and of the *o*- and *m*-chloro- and bromo-toluenes, will be submitted later.

I have again to thank the Government Grant Committee of the Royal Society, by whose assistance the cost of the apparatus used in this investigation was defrayed.

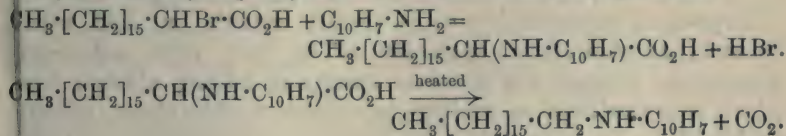
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LXXXVII.—*Preparation of Secondary Amines from Carboxylic Acids. Part II. Preparation of the Heptadecyl and Pentadecyl Derivatives of α - and β -Naphthylamine.*

By HENRY RONDEL LE SUEUR.

THE first part of this investigation (Trans., 1910, **97**, 2433) dealt with the preparation of the higher alkyl derivatives of aniline from the corresponding α -anilino-acids, and in the present communication the preparation of the heptadecyl and pentadecyl derivatives of α - and β -naphthylamine is described. When the acid resulting from the replacement of an α -hydrogen atom in stearic or palmitic acid by either the α - or β -naphthylamino-group is heated above its melting point, it readily loses carbon dioxide, and the corresponding alkyl-naphthylamine results.

The naphthylamino-acids themselves are quite readily obtained by the interaction of the α -bromo-acid and the naphthylamine; also, the yield of alkyl-naphthylamine from the acid is a good one:



EXPERIMENTAL.

Preparation of α -2-Naphthylaminostearic Acid,
 $\text{C}_{16}\text{H}_{33} \cdot \text{CH}(\text{NH} \cdot \text{C}_{10}\text{H}_7) \cdot \text{CO}_2\text{H}.$

Eleven grams of α -bromostearic acid (1 mol.) and 16 grams of β -naphthylamine ($3\frac{1}{2}$ mols.) were finely powdered, well mixed, and heated together in a flask immersed in boiling water for nine and a-half hours. The resulting product consisted of a hard cake, from

which the excess of β -naphthylamine was removed by digesting it with hot dilute hydrochloric acid, filtering, and washing with hot water. The residue of crude acid was crystallised first from ethyl acetate, and finally from alcohol, until its melting point was constant, when 9 grams of the pure acid were obtained:

0.2278 gave 6.5 c.c. N_2 (moist) at 18° and 770 mm. $N=3.34$.

$C_{28}H_{43}O_2N$ requires $N=3.29$ per cent.

α -2-Naphthylaminostearic acid is insoluble in ether, chloroform, benzene, alcohol, or ethyl acetate in the cold, is moderately soluble in boiling alcohol or ethyl acetate, and separates from the former in crystalline nodules, melting at 151 — 152° .

Heptadecyl- β -naphthylamine, $C_{17}H_{35}\cdot NH\cdot C_{10}H_7$.

The pure α -2-naphthylaminostearic acid was heated in quantities of 6 grams at a time in a small flask immersed in a metal-bath, and containing a thermometer the bulb of which dipped into the substance. As soon as the substance was completely melted, its temperature was raised rapidly to about 190° , at which point the evolution of carbon dioxide commenced. The temperature was then raised more slowly to 295 — 300° , and the heating stopped when the evolution of carbon dioxide had ceased. This took place after about twelve minutes from the time the temperature was 190° . The resulting product was dissolved in ether, the ethereal solution washed with aqueous potassium hydroxide, dried with solid potassium hydroxide, evaporated, and the residue crystallised from alcohol. The yield of amine corresponded with 70 per cent. of the theoretical:

0.1526 gave 0.4754 CO_2 and 0.1536 H_2O . $C=84.96$; $H=11.18$.

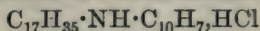
0.2554 „ 8.2 c.c. N_2 (moist) at 16° and 758 mm. $N=3.73$.

$C_{27}H_{43}N$ requires $C=85.04$; $H=11.28$; $N=3.67$ per cent.

Heptadecyl- β -naphthylamine is readily soluble in cold ether, benzene, or chloroform, sparingly so in cold light petroleum, acetone, or alcohol, and dissolves readily in boiling alcohol, from which it crystallises, on cooling, in colourless, thin plates, melting at 59 — 61° . It is insoluble in water or hydrochloric acid, but dissolves readily in concentrated sulphuric acid. The product obtained on treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*, $C_{17}H_{35}\cdot NH\cdot C_{10}H_7\cdot HCl$, was prepared by dissolving 1.3 grams of the base in 30 c.c. of ether, and saturating the resulting solution with dry hydrogen chloride. The precipitated hydrochloride was filtered and crystallised from a mixture of chloroform and light petroleum, when it was obtained in glistening,

flat needles, melting at 170—171°. It is insoluble in alcohol, ether, acetone, or light petroleum in the cold, and dissolves readily in boiling chloroform. When heated with water, it melts, but does not dissolve, and the aqueous liquid acquires a strongly acid reaction. Its purity was determined by warming it with a slight excess of *N*/10-sodium hydroxide, filtering the liberated amine, and determining the excess of sodium hydroxide in the filtrate, using methyl-orange as indicator. 0.2474 required 5.7 c.c. *N*/10-NaOH for neutralisation, whereas the same amount of



requires 5.9 c.c. *N*/10-NaOH. The free base obtained in the above titration was dried, and after crystallisation from alcohol melted at 60—61°.

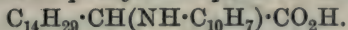
The *benzenesulphonyl* derivative, $\text{C}_{17}\text{H}_{35}\cdot\text{N}(\text{SO}_2\text{Ph})\cdot\text{C}_{10}\text{H}_7$, was prepared by heating in boiling water for two and a-quarter hours a mixture of 1 gram of the base and an equal weight of benzenesulphonyl chloride dissolved in 10 grams of dry pyridine. The resulting solution was poured on crushed ice, and when all the ice had melted, the benzenesulphonyl derivative was collected, washed, dried, and crystallised from a mixture of methyl and ethyl alcohols:

0.2336 gave 5.7 c.c. N_2 (moist) at 16° and 780 mm. $\text{N} = 2.92$.

$\text{C}_{33}\text{H}_{47}\text{O}_2\text{NS}$ requires $\text{N} = 2.69$ per cent.

Heptadecyl-β-naphthylbenzenesulphonamide is readily soluble in ether, chloroform, light petroleum, or benzene in the cold, and also in warm alcohol, from which it separates, on cooling, in stellar groups of long needles, melting at 51—52°.

Preparation of α-2-Naphthylaminopalmitic Acid,



Thirty grams of α-bromopalmitic acid (1 mol.) and 45 grams of β-naphthylamine ($3\frac{1}{2}$ mols.) were heated together in a flask immersed in boiling water for twenty-nine hours, and the product was worked up exactly as described for the preparation of the corresponding naphthylaminostearic acid (p. 827). The acid was purified by crystallisation from alcohol, and was obtained in nodules of small needles, melting at 154—155°. It is insoluble in ether, light petroleum, chloroform, benzene, or acetone in the cold, and moderately soluble in boiling alcohol. The weight of pure acid obtained corresponded with a 74 per cent. yield of the theoretical:

0.2272 gave 7.3 c.c. N_2 (moist) at 20° and 746 mm. $\text{N} = 3.61$.

$\text{C}_{26}\text{H}_{39}\text{O}_2\text{N}$ requires $\text{N} = 3.53$ per cent.

Pentadecyl- β -naphthylamine, $C_{15}H_{31} \cdot NH \cdot C_{10}H_7$.

The α -2-naphthylaminopalmitic acid was heated in quantities of 6 grams, as described for the preparation of heptadecyl- β -naphthylamine. The duration of the heating and the course of the decomposition were similar in the two cases. The crude amine was dissolved in ether, the ethereal solution washed with aqueous potassium hydroxide, dried with solid potassium hydroxide, and the residue left after evaporation of the ether crystallised from alcohol:

0.1712 gave 0.5342 CO_2 and 0.1700 H_2O . $C = 85.09$; $H = 11.03$.

0.2226 „ 7.4 c.c. N_2 (moist) at 17° and 770 mm. $N = 3.91$.

$C_{25}H_{39}N$ requires $C = 84.99$; $H = 11.05$; $N = 3.96$ per cent.

Pentadecyl- β -naphthylamine is readily soluble in ether, acetone, light petroleum, chloroform, or benzene in the cold, sparingly soluble in cold alcohol, but dissolves readily on heating, and crystallises from this solvent in colourless, glistening plates, melting at $53-54^\circ$. It is insoluble in water or hydrochloric acid, but dissolves readily in concentrated sulphuric acid. The product obtained by treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

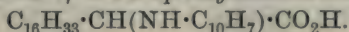
The *hydrochloride*, $C_{15}H_{31} \cdot NH \cdot C_{10}H_7 \cdot HCl$, was obtained by passing dry hydrogen chloride into an ethereal solution of the amine, and crystallising the precipitated hydrochloride from a mixture of chloroform and light petroleum. It forms glistening, flat needles, melting at $176-177^\circ$. It is insoluble in alcohol, ether, light petroleum, or acetone in the cold, and dissolves readily in hot chloroform. When heated with water, it melts, but does not dissolve, and the aqueous liquid acquires a strongly acid reaction. The hydrochloride was titrated as described for the hydrochloride of heptadecyl- β -naphthylamine, when it was found that 0.3100 required 7.6 c.c. $N/10$ -NaOH for neutralisation, using methyl-orange as indicator, whereas the same weight of $C_{15}H_{31} \cdot NH \cdot C_{10}H_7 \cdot HCl$ requires 7.9 c.c. $N/10$ -NaOH.

The *benzenesulphonyl* derivative, $C_{15}H_{31} \cdot N(SO_2Ph) \cdot C_{10}H_7$, was obtained by heating in a flask immersed in boiling water a solution of 1 gram of the amine and 1.5 grams of benzenesulphonyl chloride in 10 c.c. of dry pyridine for three hours. The product was worked up as described for the preparation of the benzenesulphonyl derivative of heptadecyl- β -naphthylamine. The substance is readily soluble in ether, chloroform, light petroleum, or benzene in the cold, is sparingly soluble in cold alcohol, but dissolves readily on heating, and crystallises from this solvent in small needles, melting at $50.5-51.5^\circ$:

0.2544 gave 6.4 c.c. N_2 (moist) at 16° and 768 mm. $N = 2.96$.

$C_{31}H_{43}O_2NS$ requires $N = 2.84$ per cent.

Preparation of α -1-Naphthylaminostearic Acid,



Thirty grams of α -bromostearic acid (1 mol.) and 45 grams of α -naphthylamine ($3\frac{1}{2}$ mols.) were heated in a flask immersed in boiling water for twelve hours. The resulting product was digested with hot dilute hydrochloric acid to remove excess of naphthylamine, and the aqueous liquid filtered from the crude acid. The acid was dissolved in ether, the ethereal solution washed first with dilute hydrochloric acid, then with water, dried, evaporated, and the residue crystallised from light petroleum (b. p. $100-120^\circ$), when it was obtained in small, glistening, lenticular plates, melting at $69-70^\circ$. It is readily soluble in alcohol, ether, chloroform, benzene, or acetone in the cold, and is sparingly soluble in cold light petroleum. The yield obtained was 56 per cent. of the theoretical:

0.2340 gave 6.9 c.c. N_2 (moist) at 16.5° and 770 mm. $N = 3.47$.

$C_{28}H_{43}O_2N$ requires $N = 3.29$ per cent.

Heptadecyl- α -naphthylamine, $C_{17}H_{35} \cdot NH \cdot C_{10}H_7$.

This amine was prepared by heating α -1-naphthylaminostearic acid, as described for the preparation of the other amines, and was purified by crystallisation from alcohol:

0.1632 gave 0.5086 CO_2 and 0.1652 H_2O . $C = 84.99$; $H = 11.24$.

0.2274 „ 7.6 c.c. N_2 (moist) at 18° and 752 mm. $N = 3.82$.

$C_{27}H_{43}N$ requires $C = 85.04$; $H = 11.28$; $N = 3.67$ per cent.

Heptadecyl- α -naphthylamine is readily soluble in ether, light petroleum, chloroform, or benzene in the cold, is moderately soluble in boiling alcohol, and crystallises from this solvent in white nodules, melting at $53-55^\circ$. It is insoluble in water and hydrochloric acid, but dissolves readily in concentrated sulphuric acid. The substance obtained by treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*, $C_{17}H_{35} \cdot NH \cdot C_{10}H_7 \cdot HCl$, was prepared by saturating with dry hydrogen chloride a solution of 1 gram of the amine in 30 c.c. of ether. Light petroleum (15 c.c.) was then added, and the ether evaporated, when, on cooling, the hydrochloride separated out in lenticular plates, which, after crystallisation from light petroleum, melted at $96-97^\circ$. The substance is insoluble in ether, light petroleum, or acetone in the cold, but readily dissolves in cold chloroform. It melts, but does not dissolve, in hot

water, and the liquid becomes strongly acid. Its purity was determined as described for the other hydrochlorides. 0.3222 required 7.5 c.c. $N/10\text{-NaOH}$ for neutralisation, using methyl-orange as indicator, whereas the same weight of the compound $\text{C}_{17}\text{H}_{35}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7\cdot\text{HCl}$ requires 7.7 c.c. $N/10\text{-NaOH}$.

The *benzenesulphonyl* derivative, $\text{C}_{17}\text{H}_{35}\cdot\text{N}(\text{SO}_2\text{Ph})\cdot\text{C}_{10}\text{H}_7$, was prepared from the amine and benzenesulphonyl chloride, as described for the preparation of the other benzenesulphonyl derivatives. It is readily soluble in ether, chloroform, benzene, or acetone in the cold, is sparingly soluble in cold alcohol, and crystallises from this solvent in nodular aggregates of needles, melting at $66\text{--}68^\circ$:

0.2626 gave 6.5 c.c. N_2 (moist) at 14.5° and 764 mm. $\text{N}=2.92$.

$\text{C}_{33}\text{H}_{47}\text{O}_2\text{NS}$ requires $\text{N}=2.69$ per cent.

Preparation of α -1-Naphthylaminopalmitic Acid,
 $\text{C}_{14}\text{H}_{29}\cdot\text{CH}(\text{NH}\cdot\text{C}_{10}\text{H}_7)\cdot\text{CO}_2\text{H}$.

This acid was prepared by the interaction of α -bromopalmitic acid and α -naphthylamine, the method being in every way similar to that used for the preparation of α -1-naphthylaminostearic acid. It is readily soluble in alcohol, ether, chloroform, benzene, or acetone in the cold, is sparingly soluble in cold light petroleum, and crystallises from this solvent in glistening, slender needles, melting at $72\text{--}73^\circ$:

0.1684 gave 0.4846 CO_2 and 0.1482 H_2O . $\text{C}=78.48$; $\text{H}=9.78$.

0.2354 „ 7.5 c.c. N_2 (moist) at 17° and 758 mm. $\text{N}=3.69$.

$\text{C}_{26}\text{H}_{39}\text{O}_2\text{N}$ requires $\text{C}=78.59$; $\text{H}=9.82$; $\text{N}=3.53$ per cent.

Pentadecyl- α -naphthylamine, $\text{C}_{15}\text{H}_{31}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$.

This amine was obtained by heating α -1-naphthylaminopalmitic acid, and working up the product as described for the preparation of the other amines. It was purified by crystallisation from alcohol:

0.1478 gave 0.4600 CO_2 and 0.1446 H_2O . $\text{C}=84.88$; $\text{H}=10.87$.

0.2148 „ 7.3 c.c. N_2 (moist) at 17.5° and 752 mm. $\text{N}=3.89$.

$\text{C}_{25}\text{H}_{39}\text{N}$ requires $\text{C}=84.99$; $\text{H}=11.05$; $\text{N}=3.96$ per cent.

Pentadecyl- α -naphthylamine is readily soluble in ether, benzene, chloroform, or acetone in the cold, is only sparingly so in cold alcohol, and crystallises from this solvent in nodular aggregates of flat needles, melting at $47\text{--}48^\circ$. The product obtained by treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*, $\text{C}_{15}\text{H}_{31}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7\cdot\text{HCl}$, was obtained from

pentadecyl- α -naphthylamine by the method used for the preparation of the hydrochloride of heptadecyl- α -naphthylamine, and was purified by crystallisation from light petroleum. It dissolves readily in cold chloroform, is sparingly soluble in ether or light petroleum in the cold, and crystallises from the latter solvent in flat needles, melting at 92—94°. 0.3354 required 8.34 c.c. $N/10$ -NaOH for neutralisation, using methyl-orange as indicator, whereas the same amount of the compound $C_{15}H_{31}\cdot NH\cdot C_{10}H_7\cdot HCl$ requires 8.61 c.c. $N/10$ -NaOH.

The *benzenesulphonyl* derivative was prepared by the interaction of the amine and benzenesulphonyl chloride in pyridine solution, and was purified by crystallisation from alcohol, when it was obtained in flat needles, melting at 68—69°. It dissolves readily in ether, chloroform, benzene, or acetone in the cold, and is sparingly soluble in cold alcohol:

0.2550 gave 6.1 c.c. N_2 (moist) at 10° and 752 mm. $N=2.83$.

$C_{31}H_{43}O_2NS$ requires $N=2.84$ per cent.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant, which has, in part, defrayed the expenses of this investigation.

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LXXXVIII.—*Chemical Action Induced by Cathode Rays and Canal Rays.*

By EDGAR PHILIP PERMAN.

THE object in undertaking this work was twofold. In the first place it was thought that canal rays, and possibly cathode rays, might effect a transmutation of elements of the kind described by Ramsay as produced by the action of radium emanation. In the second place, it was proposed to extend our knowledge of the ordinary chemical changes caused by these rays.

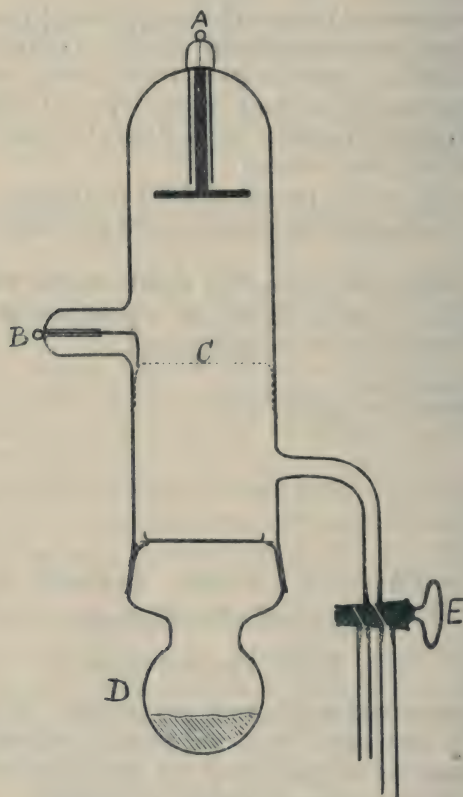
Attempts to Effect Transmutation of the Elements. Action of Canal Rays on Copper Sulphate.

Canal rays were produced in a tube as shown in the diagram (Fig. 1) with aluminium electrodes *A*, *B*. The diaphragm *C* was of fine copper gauze, and was pushed up the tube until in contact

with *B*. *D* was a ground glass stopper, on the top of which rested a perforated copper tray; on this tray the substance to be examined was placed. The tube was dried by phosphoric oxide placed at the bottom of *D*, and was exhausted by a rotary mercury pump through the stopcock *E*.

Some specially purified anhydrous copper sulphate (free from lithium) was placed on the tray, and submitted to the action of

FIG. 1.

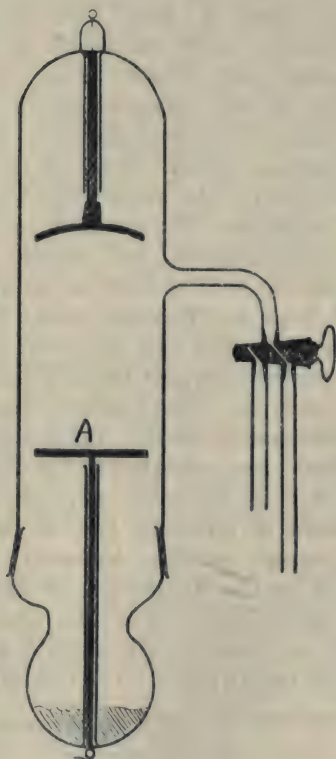


the rays for six hours. A strong beam could be seen the whole time. At first the beam was of a bluish-white colour, and showed the air line spectrum, but afterwards it became red and showed a strong hydrogen spectrum. The experiment was occasionally interrupted by admitting dry air and re-pumping. A powerful induction coil was used, and four large accumulator cells. After six hours' action, the copper sulphate was dissolved in water, the copper removed by hydrogen sulphide, the filtrate evaporated to a small

bulk, and tested by the spectroscope. No lithium or other metal was detected.

Copper as Cathode.—A plate of electrolytic copper was placed on the aluminium cathode of a tube (Fig. 2), and subjected to the discharge for six hours. In these conditions the copper is constantly giving off electrons, and in a sense may be said to be radioactive. The copper was then dissolved in nitric acid, the solution evaporated to dryness, and the residue ignited to convert

FIG. 2.



it into copper oxide. This was well washed and filtered, the filtrate evaporated to small bulk, and tested by the spectroscope. Nothing was found but a trace of sodium.

Thorium as Cathode and as Anode.—Some thorium powder was placed at the lower end of a small vacuum tube with a capillary portion in the middle. After clearing out the adsorbed gases, the thorium was made cathode, and the discharge passed for an hour; a feeble hydrogen spectrum was seen. The thorium was then made

Chemical Action of Canal Rays.

Many investigations have been made, by Goldstein, Schmidt, Sterba, and others, of the chemical action induced by cathode rays. I have, therefore, chiefly confined my attention to the action of canal rays.

Action of Canal Rays on Cuprous Oxide, Litharge, Lead Sulphide, and Chromium Sesquioxide.

(a) *In Air*:—A small quantity of the oxide was rubbed over a circular piece of paper; this was then exposed to the rays (Fig. 1). In the case of cuprous oxide and litharge, rapid oxidation occurred; in about fifteen minutes the cuprous oxide was converted into cupric oxide, and the litharge into peroxide, as shown by the colour. Lead sulphide, when treated in the same way, was slightly oxidised, whilst chromium sesquioxide was not affected. On substituting porcelain for paper, the results were the same.

(b) *In Oxygen*:—With the above-mentioned substances the same effect was produced as in air, except that the oxidation was slightly quicker.

(c) *In Coal Gas on Cupric Oxide and Lead Peroxide*:—The reverse action was then tried in order to see whether the rays would reduce in a reducing gas like coal gas. There was a slight reduction, but it was not at all equal to the amount of oxidation caused in air or oxygen.

(d) *In Hydrogen*:—The same substances gave a similar result. The hydrogen was prepared from aluminium and aqueous sodium hydroxide.

Canal Rays in Air on Ferric Chloride, Mercuric Chloride, and Potassium Chlorate:—These substances were found to be reduced by the rays in air, especially the mercuric chloride, which gave a black coloration with ammonia after a few minutes' action. Ferric chloride, after the action of the rays, gave a blue coloration with potassium ferrocyanide, and potassium chlorate gave a precipitate with silver nitrate. The materials were placed in a shallow glass dish for the experiment. Their purity was carefully tested.

Canal Rays in Hydrogen on Ferric Chloride and Iron Alum:—There was a slight reduction, the extent of the change being about the same as in presence of air.

Canal Rays in Coal Gas on Cuprous Oxide, Potassium Chlorate, and Silver Oxide:—There was no change, except in the case of potassium chlorate, which was slightly reduced.

Canal Rays in Air on Metallic Silver, Mercury, Magnesium, and Copper:—The silver, copper, and magnesium were examined in

the form of foil, and the mercury was placed in a shallow glass dish. The copper and the silver were slightly oxidised, the magnesium and mercury remaining perfectly bright.

Canal Rays in Oxygen on Mercury and Aluminium:—There was no oxidation.

Canal Rays in Nitrogen on Magnesium:—It was thought that magnesium nitride might be formed. After exposure to the rays for thirty minutes, the magnesium was dissolved in dilute hydrochloric acid, the magnesium removed by sodium carbonate, and the filtrate tested for ammonia by Nessler's solution. None was found.

Canal Rays in Coal Gas on Sulphur:—The rays in coal gas were allowed to fall on powdered sulphur in a glass dish. Some of the sulphur was vaporised, and deposited on the sides of the tube; no hydrogen sulphide could be found. It should be noted that a large proportion would have to be formed in order to be detected.

Canal Rays in Nitrogen and Hydrogen (Mixed):—Traces of ammonia were found in the gases after passing the rays for a few minutes. The test was made by admitting air free from ammonia to the tube, and then pumping out the gases through dilute acid and testing with Nessler's solution. As the ordinary electric discharge will cause nitrogen and hydrogen to combine, there is no proof that ammonia is formed by the action of the rays.

Canal Rays on Hydrocarbons:—A glass plate was smeared with vaseline, and exposed to the action of the rays in air. In a few minutes the beam acquired a strong red tint, and showed the hydrogen spectrum. The vaseline became darkened in colour, no doubt owing to the separation of carbon.

Direct Oxidising Action of Canal Rays.—Schmidt (*Ann. Physik*, 1902, [iv], 9, 703) states that canal rays do not exercise any direct oxidising action, for he found that a copper plate was so much oxidised in the shadow of a solid object placed in the rays as when directly exposed. In order to confirm this point, the following experiments were made:

(1) Some cuprous oxide was rubbed on a circular piece of paper 3.5 mm. in diameter, and a strip of paper 5 mm. wide was fixed 12.5 mm. above it. It was then subjected to the action of the rays. The cuprous oxide directly under the strip remained unaltered; there was a sharp line of demarcation.

(2) A similar strip of paper was fixed 25 mm. above the cuprous oxide. After exposure to the rays there was some difference of colour below the strip, but no sharp boundary line.

(3) A paper diaphragm with a triangular hole in the centre was fixed 12.5 mm. above the cuprous oxide. On exposure to the rays it gave an enlarged but fairly sharp triangle on the cuprous

oxide. The 9 mm. side of the triangle became 12 mm. on the oxide.

(4) The diaphragm was fixed 25 mm. above the cuprous oxide. An enlarged but ill-defined triangle was formed on the oxide. It should be noted that there was not a distinct beam in this experiment, owing to the presence of the paper diaphragm. In all these experiments the gauze cathode was 5 cm. above the cuprous oxide.

It is clear from these experiments that oxidation is much more rapid in the direct path of the beam, but that there is some scattering of the rays, or of the effect of the rays. As an explanation of this, I suggest that in addition to the main beam of canal rays travelling down the centre of the tube, there are others travelling crosswise, and that these latter cause the scattering effect. The oxidation does not appear to be due to the formation of ozone, for mercury exposed to the rays in oxygen remained perfectly bright. Tests for ozone were also made by admitting air, drawing off the gases through potassium iodide solution, and adding starch solution; this was repeated twice with the same solution, but without result. According to the ideas of Ramsay and others, the elements in a compound are held together by electrons, and this may be represented diagrammatically in the case of cuprous oxide by the formula $\text{Cu}\cdot\text{O}\cdot\text{Cu}$. Now the canal rays appear to be atoms minus electrons; the rays in oxygen will therefore have the power of dragging more electrons from the copper, and forming cupric oxide, $\text{Cu}\cdot\text{O}$.

Canal Rays on Potassium Chloride:—After four hours the crystals had acquired a distinct violet colour, as found to be produced by cathode rays by Sterba (*Monatsh.*, 1907, **28**, 397) and others. The coloured crystals were corked up in a test-tube and exposed to diffused daylight. After a few weeks the colour had entirely disappeared. From the observations of Sterba, the colour would appear to be due to a slight reduction of the salt to the metal. The canal rays probably produce the same effect by bombarding the molecules.

Canal Rays on Calcium Chloride:—Anhydrous calcium chloride was treated in the same way as potassium chloride, but no coloration was produced.

Velocity of Chemical Action caused by Canal Rays:—A quantitative experiment was made with potassium chlorate. About two grams were placed in a shallow glass dish and exposed to the rays for three hours. There was a loss of weight of 0.5 milligram. The error of weighing was certainly not more than 0.1 milligram.

Cause of Chemical Action:—Most of the chemical action observed is merely decomposition, and is no doubt caused by the bombard-

ment of the substance by the rays. It is practically impossible to distinguish this from the superficial heating effect. The oxidation effects, however, are cases of synthesis; the formation of lead peroxide cannot be due to the heating effect of the rays, and does not appear to be caused by secondary action; the oxidation is probably brought about by the direct action of the positive rays. It should be observed that the measurable heating effect in these experiments was never very great; the lower end of the tube became warm (about 30°), but was never strongly heated. The battery power used was sufficient to give a strong beam of canal rays, but insufficient to produce much rise of temperature. The superficial heating is another matter.

Effect on Metal Diaphragm:—A copper gauze diaphragm was generally employed, as it was found to give a distinct beam most readily. It was always found to be oxidised on the under surface and bright above. A nickel diaphragm was affected in the same way. A diaphragm of aluminium, however, was oxidised on the upper surface, and not below.

Summary.

The chief conclusions arrived at are:

- (a) Neither canal rays nor cathode rays produce any transmutation of the elements.
- (b) Canal rays in air or oxygen have a strong oxidising action.
- (c) The oxidising action appears to be mostly direct, but is accompanied by a scattering effect.
- (d) Many substances are decomposed by the action of canal rays independently of the nature of the gas in which the rays are produced.

I wish to express my indebtedness to the Royal Society for a grant covering the expenses of this work.

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CARDIFF.

LXXXIX.—*The Element* $\text{Cu} \mid \text{Cu}_2\text{O}$ *Alkali* $\mid \text{H}_2$ *at* 0° .

By ARTHUR JOHN ALLMAND.

IN a recent paper (Trans., 1909, 95, 2151) the results of *E.M.F.* measurements at room temperature of combinations containing the electrode system $\text{Cu} \mid \text{Cu}_2\text{O}$ alkali were given. Using calculated values for the potential of the electrode $\text{Pt} \mid \text{H}_2 \mid$ alkali, the author

was able to obtain figures for the *E.M.F.* of the combination $\text{Cu} | \text{Cu}_2\text{O}$ alkali $| \text{H}_2$.

They were:

with $N/10$ -alkali 0.473 volt

with N -alkali 0.466 volt,

the mean value being 0.469 volt.

Using Nernst's theorem, the *E.M.F.* of the same system was then calculated from purely thermal data for a temperature of 17° , and the figure 0.472 volt obtained. As Nernst himself has pointed out in similar cases, however (*Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 247), such a calculation is open to objection, as it involves an extrapolation to low temperatures of the specific heat of super-cooled water, a quantity which is not known with any degree of accuracy. On that account, he prefers to carry out his calculations for a temperature of 0° , whereby he is able to introduce ice instead of water as one of the resultants of the reaction. The author was fully alive to this objection, and only made the calculation when he had assured himself that in the analogous case dealt with by Nernst the difference involved was only about 0.01 volt. It was, however, considered advisable to also measure the combination at 0° , in order that a stricter comparison might be made. This has now been done. One electrode only was set up, the electrolyte being N - NaOH . The electrode vessel used has already been described (*loc. cit.*). After shaking for a few days, measurements were made against a normal calomel electrode, first at room temperature, and then in ice, using the thermostat described in the next paper.

The results obtained were:

Current in cell

$\text{Hg} | \text{HgCl } N\text{-KCl} | N\text{-NaOH } \text{Cu}_2\text{O} | \text{Cu}$ 0.610 volt at 16°
 $\text{Hg} | \text{HgCl } N\text{-KCl} | N\text{-NaOH } \text{Cu}_2\text{O} | \text{Cu}$ 0.592 „ 0° .

For the calculation of the $\text{Cu} | \text{Cu}_2\text{O}$ alkali single potential, one can use the following figures:

$\text{Hg} | \text{HgCl } N\text{-KCl}$ +0.282 volt at 16°

$\text{Hg} | \text{HgCl } N\text{-KCl}$ +0.272 „ 0° ,

and

$N\text{-KCl} | N\text{-NaOH}$ 0.020 volt at 16°

$N\text{-KCl} | N\text{-NaOH}$ 0.021 „ 0° ,

the KCl solution being the more negative.

One obtains:

$\text{Cu} | \text{Cu}_2\text{O } N\text{-NaOH}$ -0.348 volt at 16°

$\text{Cu} | \text{Cu}_2\text{O } N\text{-NaOH}$ -0.341 „ 0° .

It might be mentioned that the author's previous measurements gave (at room temperature) for the above cell:

0.606 volt using sodium hydroxide

0.613 „ „ „ potassium hydroxide,

and for the single potential $\text{Cu} \mid \text{Cu}_2\text{O}$ *N*-alkali, -0.344 volt with sodium hydroxide, and -0.346 volt with potassium hydroxide.

To get the required *E.M.F.*, it is now necessary to know the potential of the electrode system $\text{H}_2 \mid \text{N-NaOH}$ at 0° . Unfortunately, existing figures on the potentials of hydrogen electrodes in alkaline solutions are untrustworthy, which is, indeed, the reason why the author has been compelled to use an auxiliary calomel electrode in this and other work. But in addition to that, we are in possession of no experimental data as to the temperature-coefficient of the hydrogen electrode, whether in acid or alkaline solution. The required potential can, therefore, only be calculated by a somewhat roundabout method. One proceeds as follows.

Using the methods indicated by Nernst (*Thermodynamics and Chemistry*, pp. 113—114), we obtain for the *E.M.F.* of the $\text{H}_2\text{-O}_2$ cell:

1.226 volt at 25°

1.232 „ „ „ 18°

1.249 „ „ „ 0° .

We now set $\text{H}_2 \mid \text{N-H}^+$ ion $= 0.0$ volt at 18° . It may be noted in passing that this assumption, or rather the assumption that the difference of the potentials at 18° of the *N*-calomel electrode and the $\text{H}_2 \mid \text{N-H}^+$ ion is 0.283 volt, is none too certain a one. The error may amount to two to three millivolts. The single values from which it is deduced (*Zeitsch. physikal. Chem.*, 1900, **35**, 302) differ considerably amongst themselves. They involve, in most cases, an uncertain correction for a liquid potential difference, and a further correction for the H^+ ion concentration of the solution used, a correction which, in view of the results of Noyes and Sammet (*J. Amer. Chem. Soc.*, 1902, **24**, 758; 1903, **25**, 167), also appears uncertain. Further, they refer to different temperatures. The measurements of Smale and Neumann were carried out at $17\text{--}18^\circ$, whilst Wilsmore's figures give the potential difference between the *N*-calomel electrode at 25° and the $\text{H}_2 \mid \text{N-H}^+$ ion electrode at the same temperature. Other figures for H_2 -electrodes at 25° are given in Ostwald-Luther-Drucker's *Physiko-Chemische Messungen* (p. 445), and Luther and Michie (*Zeitsch. Elektrochem.*, 1908, **14**, 826) assume certain values for H_2 -electrode potentials at 18° . A comparison of all these values shows that the different measurements with H_2 -electrodes in sulphuric acid solutions mostly agree to within 2 millivolts, but that potentials deduced from measurements with

hydrochloric acid as an electrolyte show much larger discrepancies. Assuming, however, that $H_2|N\text{-}H^+$ ion = 0.0 volt at 18°, and that *N*-sodium hydroxide is dissociated to the extent of 72 per cent. at that temperature, we can deduce that $H_2|N\text{-}NaOH = -0.810$ volt at 18°: and consequently, $O_2|N\text{-}NaOH = 1.232 - 0.810 = +0.422$ volt at 18°.

In the course of his determination of the *E.M.F.* of the $H_2\text{-}O_2$ cell (*Zeitsch. physikal. Chem.*, 1906, **55**, 465), Lewis calculated the temperature-coefficient of the electrode $O_2|N\text{-}OH'$ ion as -0.00079 volt per degree at room temperature. His value for the *E.M.F.* of the cell appears to be a few millivolts too low. If we correct for this, and for a slight difference between the value for the potential $Ag|N\text{-}Ag^+$ used by him and the value now recognised, we get -0.000763 volt per degree. Now this is the temperature-coefficient of the oxygen electrode in a solution of *N*- OH' ion concentration. It will be slightly different in *N*-sodium hydroxide. If we take (as before) the OH' ion concentration in such a solution as 0.72, we calculate quite readily that $O_2|N\text{-}OH'$ ion at 18° = +0.414. If now *U* be the decrease of total energy per gram-equivalent of the reaction,



and *x* the temperature-coefficient of the oxygen electrode in *N*-sodium hydroxide, we have

$$U = 0.422 - 291 \cdot x.$$

Also:

$$U = 0.414 - 291 (-0.000763).$$

Whence

$$x = -0.00072 \frac{\text{volt}}{\text{degree}}$$

Therefore:

$$\begin{aligned} O_2 | N\text{-}NaOH \text{ at } 0^\circ &= +0.422 + 18 (0.00072) \\ &= +0.4350 \text{ volt.} \end{aligned}$$

Whence

$$\begin{aligned} H_2 | N\text{-}NaOH \text{ at } 0^\circ &= -1.249 + 0.435 \\ &= -0.814 \text{ volt.} \end{aligned}$$

Similarly, we calculate:

$$\begin{aligned} O_2 | N\text{-}NaOH \text{ at } 25^\circ &= +0.4170 \text{ volt.} \\ H_2 | N\text{-}NaOH \text{ „ } 25^\circ &= -1.226 + 0.417 \\ &= -0.809 \text{ volt.} \end{aligned}$$

And we obtain as the temperature-coefficient of the hydrogen electrode in alkaline solution,

$$\frac{0.814 - 0.809}{25} = +0.0002 \frac{\text{volt}}{\text{degree}}.$$

Combining now the values for the H₂|N-NaOH and Cu|Cu₂O N-NaOH electrodes at 0° and 18°, we obtain for the *E.M.F.* of the cell Cu|Cu₂O alkali|H₂:

$$\begin{aligned} \text{at } 0^\circ & (0.814 - 0.341) = 0.473 \text{ volt} \\ 18^\circ & (0.810 - 0.349) = 0.461 \text{ ,,} \end{aligned}$$

and as its temperature-coefficient:

$$- 0.00066 \frac{\text{volt}}{\text{degree}}.$$

From these data we can readily calculate the total energy change at 18° of the reaction:



We have:

$$U = A - T \frac{dA}{dT}$$

And

$$\begin{aligned} A &= 96540 \times 2 \times 0.461 \text{ joules} \\ - T \frac{dA}{dT} &= 96540 \times 2 \times 291 \times 0.00066 \text{ joules.} \end{aligned}$$

Hence

$$\begin{aligned} U &= \frac{96540 \times 2}{4.19} (0.461 + 0.194) \text{ calories} \\ &= 27530 \text{ calories.} \end{aligned}$$

This agrees very well with the calorimetrically determined value, 27,400 calories.

In carrying out the *E.M.F.* calculation for 0° according to Nernst's method, we make use of the following data:

$$\left. \begin{aligned} [\text{H}_2, \text{O}] &= 68200 \text{ cal.} + [\text{H}_2\text{O}] \\ [2\text{Cu}, \text{O}] &= 40800 \text{ cal.} + [\text{Cu}_2\text{O}] \\ [\text{H}_2\text{O}]_{\text{water}} &= 1580 \text{ cal.} + [\text{H}_2\text{O}]_{\text{ice}} \end{aligned} \right\} \text{all at } 17^\circ.$$

The following molecular specific heats are involved: [H₂]=6.8; [H₂O]_{ice}=9.5; [Cu₂O]=15.9; [2Cu]=12.1.

We deduce for the reaction:



which is the one which takes place in the cell in question, that

$$Q_{290^\circ} = 28980 \text{ calories.}$$

Calculating in the usual manner, we find that

$$\begin{aligned} \beta &= -0.004 \\ \text{and } Q_0 &= 28300. \end{aligned}$$

Whence

$$\begin{aligned} E_{273} &= \frac{0.0001983 \times 273}{2} \left(\frac{28300}{4.571 \times 273} - 1.75 \log 273 + \right. \\ &\quad \left. \frac{0.004 \times 273}{4.571} - 1.6 \right) \\ &= 0.462 \text{ volt.} \end{aligned}$$

We have found experimentally, 0.473 volt. The difference between found and calculated figures is, therefore, eleven millivolts. The agreement is not as good as previously seemed, but can, nevertheless, be regarded as satisfactory.

Summary of Results.

(a) The *E.M.F.* of the element $\text{Cu}|\text{Cu}_2\text{O alkali}|\text{H}_2$ at 0° is 0.473 volt, whilst the value calculated by the Nernst theorem is 0.462 volt.

(b) The following electrode temperature-coefficients hold good:

O_2	$ $	$N\text{-OH}'$	$=$	-0.00076	volt per degree
O_2	$ $	$N\text{-NaOH}$	$=$	-0.00072	" " "
H_2	$ $	$N\text{-NaOH}$	$=$	$+0.0002$	" " "

(c) The heat of reaction at 18° of the reaction



is electrochemically determined, and agrees well with the calorimetric value.

The author is much obliged to Professor Donnan for his interest in this work.

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XC.—A Standard Electrode with Alkaline Electrolyte: $\text{Hg}|\text{HgO Alkali}$.

By FREDERICK GEORGE DONNAN and ARTHUR JOHN ALLMAND.

IN a recently published investigation (*Zeitsch. Elektrochem.*, 1910, 16, 254) of the electromotive behaviour of the oxides of mercury in alkaline electrolytes, one of us was able to show that the two mercuric oxides, yellow and red, are identical—a view the correctness of which had been challenged—and that all discrepancies previously observed in their electromotive behaviour could be ascribed to the use of samples containing particles of different degrees of fineness of division. At the same time, the close agreement between the results given by different specimens of oxide justified the continuance of the work, using more refined methods of measurement, in the hope that well-defined alkaline normal electrodes would result. An account of this work is here presented, and it will be seen that the expectations have been justified.

Plan of Work.—It was decided to carry out measurements on two distinct samples of oxide. As electrolytes were chosen *N*-sodium hydroxide and *N*-potassium hydroxide, which had previously (*loc. cit.*) given unexpectedly varying potential values, and *N*/10-sodium hydroxide. The corresponding auxiliary electrodes were *N*- and *N*/10-calomel electrodes. 0° and 25° were selected as working temperatures.

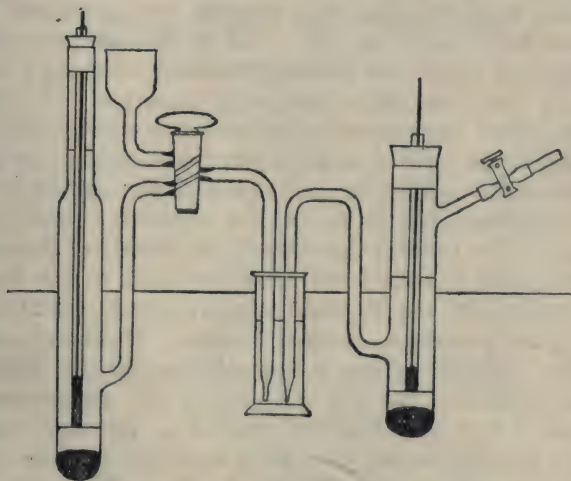
Materials, Apparatus, and Methods of Measurement.—The two samples of mercuric oxide used were prepared by the action of heat in one case on mercuric nitrate, and in the other on mercurous nitrate. As previously found, if either of these salts be fused in a porcelain basin and the heating be gently continued, with constant stirring and occasional cooling and gentle powdering, until no further traces of nitrogen oxides are given off, the resulting products, which are of a light reddish-brown colour, only contain a very small proportion of particles of small size, and quickly give constant electromotive systems.

The alkaline solutions were free from carbonate and prepared from clean metal. The *N*/10-sodium hydroxide was prepared by dilution of the *N*-sodium hydroxide. In all cases, of course, the solutions were carefully checked against standard acid before use.

The thermostat used at 25° allowed of a regulation of $\pm 0.04^\circ$. For the measurements at 0°, an arrangement of two rectangular boxes, one inside the other, was employed. The inner vessel was made of tinned iron, and the outer one of wood, well coated externally with layers of felt. The interspace was packed with cotton wool. This outer vessel was considerably higher than the inner, and even when the latter was supported inside on corks and cotton wool, there was space for a thick layer of cotton wool between the tops of the electrodes and the lid of the outer box. The inner vessel was packed full with a mixture of finely ground ice and water, and could be kept below 0.5° for several days, the exact time depending, of course, on the external temperature and the proportion of ice present.

The type of electrode vessel used, one described by Wilsmore (*Zeitsch. Elektrochem.*, 1904, **10**, 685), is shown in the figure. Mercury was poured in to the depth of 1—2 cm., and on this was placed a layer of the oxide. The vessel was then filled with the electrolyte up to the shoulder, and the rubber stopper and tube making connexion with the mercury firmly inserted. The displaced alkali flowed out through the tap, which was at once closed. The rubber stopper and glass rubber junctions were then waxed over, and the connecting tube washed free from alkali by means of the water placed in the cup. The half element was then placed in the

thermostat, and remained there until all measurements with it had been made. The calomel electrode vessels were of the ordinary type (see figure). Several electrodes of each kind were made up at different times. The authors can confirm the observation made by Lewis and Sargent (*J. Amer. Chem. Soc.*, 1909, **31**, 362) on the differences between the potential values obtained when, on the one hand, the mercurous chloride depolariser has been only shaken with the potassium chloride solution, and, on the other, previously ground up into a paste with mercury and the solution, and subsequently shaken (*Physiko-Chemische Messungen*, 3rd edition, p. 443). The former electrodes, which were nearly always 0.2 m.v. more negative than the latter, undoubtedly give the more correct potential value, and were used in all the measurements of



the calomel-mercuric oxide combination. *N*-Calomel electrodes prepared in this way almost invariably agreed to within 0.2 m.v., and generally within 0.1 m.v. With *N*/10-electrodes, the variations were slightly greater. In all cases, before readings were taken, the auxiliary electrodes were compared with one another, and were only used if they agreed to within 0.1 m.v. in the case of *N*-electrodes, and 0.2 m.v. in the case of *N*/10-electrodes.

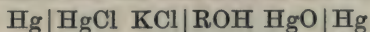
The normal cadmium element used was of the type recommended by Smith, and had been standardised in the National Physical Laboratory. Its *E.M.F.* was taken as $1.0184 - 0.0004 (t^\circ - 20)$ (see *Phil. Trans.*, 1907, A, **207**, 393).

The potentiometer was a Clark-Fisher instrument, which had been previously calibrated at the National Physical Laboratory. One mm. on its slide wire corresponded with 0.0001 volt.

The manner of carrying out a series of measurements was as follows. A stoppered bottle was filled with the same carbonate-free standard alkali as that in the mercuric oxide electrode, and was hung in the thermostat. Whilst this was being heated or cooled to the thermostat temperature, the potentials of the various calomel electrodes which had been placed in the thermostat about an hour before were compared. This was done in the ordinary way, the two opposed electrodes being measured in series with the normal cadmium element. The connecting vessel (see figure) consisted of a small glass cylinder almost entirely immersed in the thermostat. It was filled, of course, with potassium chloride of the same strength as that in the calomel electrodes, a bottle containing such a solution being continually kept in the thermostat. From the results of this comparison, two electrodes were selected for the actual measurements, and fixed ready for use. One of the mercuric oxide electrodes was then taken, and its empty vertical connecting tube filled with alkali from the bottle previously placed in the thermostat. With the end of the connecting tube in the alkali bottle, the tap was turned for an instant so as to put the electrode vessel itself in connexion with the side-tube, and thus equalise any slight pressure difference between the inside of the electrode vessel and the atmosphere. The tap was then closed, the outside of the connecting tube wiped, and the electrode vessel replaced in the thermostat, but this time with the side-tube dipping down into the cylinder containing the potassium chloride solution. Electrical connexions were made. After waiting a few minutes for all temperatures to adjust themselves, the tap was opened, and measurements were commenced. The combinations calomel i, mercuric oxide, and calomel ii, mercuric oxide, were each measured in series with, and in series against, the standard cell. Each mercuric oxide electrode was thus measured four times. By working in this way, any fluctuations in the single potential of the mercuric oxide electrode due to its being easily polarised by current passing through would be detected. As a matter of fact, no evidence of any such polarisation was found. The mean was taken of the four almost identical values for the *E.M.F.* of the combination $\text{Hg}|\text{HgCl} \text{ KCl}|\text{alkali}$ $\text{HgO}|\text{Hg}$, and it is this mean value which appears in the subsequent tables of experimental results. When the readings with an electrode were completed, the tap was closed, the side-tube carefully washed out, and the vessel placed back in its old position in the thermostat.

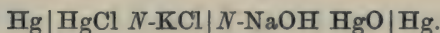
Results.

The figures obtained for the *E.M.F.*'s of the combinations



are given in volts in the following tables. Current always flows in the cell from the mercuric oxide to the calomel. The method of preparation of the oxide is indicated in each case. Sample (17) of table V is also sample (17) of the previous paper on mercuric oxides (*loc. cit.*), and was prepared by shaking up *yellow* mercuric oxide obtained from Kahlbaum with 10 per cent. sodium hydroxide at room temperature for seven weeks.

TABLE I.

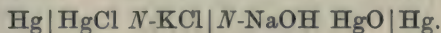


Temperature 25°.

Electrodes set up		May 26.	May 28.	May 29.	June 1.	June 6.	June 11.
From mercurous nitrate.	1		0.1540	0.1542	0.1541	0.1540	0.1540
	2		0.1542	0.1544	0.1546	0.1542	0.1544
	3		0.1538	0.1541	0.1540	0.1540	0.1540
From mercuric nitrate.	4		0.1539	0.1541	0.1540	0.1540	0.1541
	5		0.1540	0.1541	0.1540	0.1540	0.1541
	6		0.1541	0.1542	0.1542	0.1542	0.1543

Mean value 0.1541 \pm 0.00002.

TABLE II.

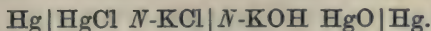


Temperature 0°.

	July 1.	July 6.
3	0.1348	0.1348
4	0.1353	0.1353
5	0.1348	0.1349
6	0.1348	0.1349

Mean value 0.1349 \pm 0.00008.

TABLE III.

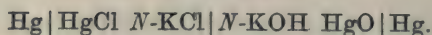


Temperature 25°.

Electrodes set up		June 20.	June 22.	June 24.	June 29.	July 4.
From mercurous nitrate.	7		0.1618	0.1620	0.1621	0.1620
	8		0.1620	0.1621	0.1621	0.1621
From mercuric nitrate.	9		0.1620	0.1617	0.1618	Broken
	10		0.1619	0.1619	0.1621	0.1620

Mean value 0.1620 \pm 0.00004.

TABLE IV.

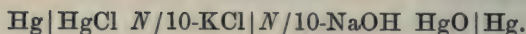


Temperature 0°.

	July 8.	July 12.
7.....	0.1431	0.1429
8.....	0.1435	0.1434
10.....	0.1432	0.1436

Mean value 0.1433 ± 0.00011 .

TABLE V.

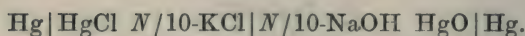


Temperature 25°.

Electrodes set up.				
July 14.		July 16.	July 19.	July 25.
From	11.....	0.1499*	0.1518	0.1514
mercurous	12.....	0.1487*	0.1505*	0.1506*
	13.....	0.1493*	0.1500*	0.1515
From	14.....	0.1523	0.1516	0.1517
mercuric	15.....	0.1518	0.1519	0.1522
	16.....	0.1509*	0.1518	0.1518
nitrate.				
Yellow				
mercuric	17.....	0.1496*	0.1490*	0.1515
	oxide.			

Mean value 0.1518 ± 0.00008 .

TABLE VI.



Temperature 0°.

	July 26.
11.....	0.1326
13.....	0.1324
14.....	0.1328
16.....	0.1326

Mean value 0.1326 ± 0.00008 .

In the calculation of the mean values and mean errors, the following readings are not taken into account:

Table I.—Those of May 28, as equilibrium had probably not completely set in.

Table III.—Those of June 22, for the same reason.

Table V.—All the readings marked with an asterisk, where equilibrium had clearly not been reached.

It is obvious from the above figures that the mercuric oxide electrode can be very exactly defined. This is particularly clear from the results at 25°. The readings at 0° were not carried out with such exact care, as the temperature-coefficient of the electrode, to ascertain which those particular measurements were undertaken,

is not appreciably affected by a small error in the *E.M.F.* determinations. It is satisfactory that the electrode made up with yellow mercuric oxide (17) gives essentially the same behaviour as those made up with the red oxide, only requiring a rather longer time to settle down. This, of course, is a confirmation of conclusions previously arrived at. The results obtained for the different combinations, and the temperature-coefficients of *E.M.F.* calculated for the same, are collected in table VII.

TABLE VII.

Element.	<i>E.M.F.</i> at 0° in volts.	<i>E.M.F.</i> at 25° in volts.	Temperature- coefficient.
<i>N</i> -Calomel <i>N</i> -KOH HgO Hg } <i>N</i> -Calomel <i>N</i> -NaOH HgO Hg }	0.1433 ± 0.00011	0.1620 ± 0.00004	+0.00075 voltage degree
<i>N</i> /10-Calomel <i>N</i> /10- NaOH HgO Hg }	0.1326 ± 0.00008	0.1518 ± 0.00008	+0.00077

It will be noticed that the temperature-coefficients are identical with *N*/10-sodium hydroxide and *N*-sodium hydroxide as electrolytes, and that the value with *N*-potassium hydroxide is only very slightly less.

The calculated errors in table VII are probable errors of the mean value; but if the electrode is to be recommended as a standard, it is also of importance to know the probable error to be expected in the setting up of any single electrode according to the above instructions. These probable errors have been calculated from the results at 25°. For electrodes with *N*-alkali electrolyte they hold good for readings made three days after setting up; with *N*/10-alkali electrodes the readings are taken eleven days after setting up. The electrode vessels are supposed to have been kept all the time at 25°:

Hg HgO <i>N</i> -NaOH	± 0.00015 volt.
Hg HgO <i>N</i> -KOH	± 0.00019 "
Hg HgO <i>N</i> /10-NaOH	± 0.00057 "

If we omit the value given by electrode (12) in table V, the mean error of setting up becomes, in the last case, ± 0.00032 volt. This last set of calculations assumes, of course, that fluctuations in the *E.M.F.*'s of the above elements are entirely due to the mercuric oxide half-element, the calomel electrode remaining constant.

From the above results we must now calculate the single potential differences and temperature-coefficients of the mercuric oxide electrodes.

Taking the potential of the *N*-calomel electrode at 18° as +0.283 volt, we will make use of Sauer's value (*Zeitsch. physikal. Chem.*, 1904, **47**, 146) for the potential of the *N*/10-calomel electrode at 18° (+0.335 volt) and Richards' values (*Zeitsch. physikal. Chem.*, 1897, **24**, 39) for the temperature-coefficients of the two electrodes (+0.00061 $\frac{\text{volt}}{\text{degree}}$ for the *N*-calomel and +0.00079 $\frac{\text{volt}}{\text{degree}}$ for the *N*/10-calomel).

Then we have:

<i>N</i> -Calomel electrode at 25°	+0.2873 volt.
<i>N</i> - " " " 0°	+0.2720 "
<i>N</i> /10-Calomel electrode at 25°	+0.3405 "
<i>N</i> /10- " " " 0°	+0.3208 "

The next step is the evaluation of the potential differences at the junction of the different electrolytes, and here we encounter the difficulty common to all calculations of this type—uncertainty as to how far the real values coincide with the calculated values. In very dilute solutions there is no reason to suppose discrepancies to occur, but in stronger solutions, where the degrees of dissociation are not so well known and may be unequal, and where, also, the ionic mobilities may be different from those at infinite dilution, it is very possible that errors may arise. For use in the Planck formula, the ionic mobilities of Na⁺, K⁺, Cl⁻, and OH⁻ were calculated for 0° and 25°, using the values for 18° and the temperature-coefficients given by Kohlrausch and von Steinwehr (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 570, 581). The values obtained are:

	l_0 .	l_{25} .
Na ⁺	24.5	51.0
K ⁺	39.4	74.5
Cl ⁻	40.0	74.3
OH ⁻	117.6	195.9

Introducing them into the Planck equations, we obtain for the liquid potential difference:

	0°.	25°.
<i>N</i> -NaOH - <i>N</i> -KCl	} 0.0209 volt	} 0.0197 volt
<i>N</i> /10-NaOH - <i>N</i> /10-KCl		
<i>N</i> -KOH - <i>N</i> -KCl		
	0.0160 "	0.0153 "

In the last case, we can also calculate on the lines indicated by Lewis and Sargent (*J. Amer. Chem. Soc.*, 1909, **31**, 363). They have pointed out that when one ion is common to the two electrolytes, the Planck equation becomes $E = \frac{RT}{F} \ln \frac{\lambda_0^1}{\lambda_0^2}$, where λ_0^1 and λ_0^2 represent the molecular conductivities of the solutions concerned at infinite dilution. As, however, the Planck equation rests on the assumption that the ionic mobilities do not vary with the concentration, and as this assumption is not always well founded,

it would be better to substitute for $\frac{\lambda_0^1}{\lambda_0^2}$, $\frac{\lambda_1}{\lambda_2}$, that is, the ratio of the conductivities of the actual solutions dealt with. In which case, the ionic mobilities entering into the calculation are those actually involved in the measurement. They have experimentally tested this method of calculation, using 0.1 and 0.2 *N*-solutions, and have obtained very good agreement. But whether the equation can be advantageously applied to more concentrated solutions, is yet doubtful.

For the purpose of the present calculation, the molecular conductivities of *N*-potassium hydroxide and *N*-potassium chloride at 18° are taken as 182.5 and 98.3 respectively. Using as temperature-coefficients of conductivity, 0.0187 for potassium hydroxide and 0.0195 for potassium chloride, we obtain:

	λ for 0°.	λ for 25°.
<i>N</i> -KOH	121.1	206.4
<i>N</i> -KCl	63.8	111.7

and these figures give for the potential difference *N*-KOH—*N*-KCl:

0°.	25°.
0.0151 volt	0.0158 volt

The values differ by 0.5—0.9 m.v. from those obtained by the Planck formula. Which are the more correct, is not easy to say. According to the Planck formula, the P.D. is greater at 0° than at 25°; according to the Lewis-Sargent formula, the reverse is correct, which seems more probable. On the other hand, the latter authors themselves have both calculated and measured the potential difference at 25° between 0.1*N*-potassium hydroxide and 0.1*N*-potassium chloride and between 0.2*N*-potassium hydroxide and 0.2*N*-potassium chloride. They find 0.0165 and 0.0169 volt respectively, values which increase with the concentration, whilst the above figure for a much stronger solution is considerably lower.

Table VIII contains the values for the single potentials of the electrodes at 0° and 25°, and also their temperature-coefficients. In the case of the Hg|HgO *N*-KOH electrode, the calculation has been made, using both the Planck and the Lewis-Sargent formulæ.

TABLE VIII.

Electrode.	Potential at 0°.	Potential at 25°.	Temperature-coefficient.
Hg HgO <i>N</i> -KOH (Lewis and Sargent)	+0.1186 volt	+0.1095 volt	-0.00016 $\frac{\text{volt}}{\text{degree}}$
Hg HgO <i>N</i> -KOH (Planck)	0.1127 „	0.1100 „	-0.00011
Hg HgO <i>N</i> -NaOH	0.1162 „	0.1135 „	-0.00011
Hg HgO <i>N</i> /10-NaOH...	0.1673 „	0.1690 „	+0.00007

Several conclusions can be drawn from this table. As the tem-

perature-coefficients of the electrodes $\text{Hg}|\text{HgO } N\text{-NaOH}$ and $\text{Hg}|\text{HgO } N/10\text{-NaOH}$ are of opposite sign, whilst, on the other hand, the two combinations $\text{Hg}|\text{HgCl KCl}|\text{NaOH HgO}|\text{Hg}$ have identical temperature-coefficients, it would at first appear that some error had entered the intermediate calculation, or that faulty data had been used. This, however, is not so. The difference between the temperature-coefficients of the N - and $0.1N$ -calomel electrodes is exactly balanced by the difference between the temperature-coefficients of the N - and $0.1N$ -mercuric oxide electrodes; and, in both cases, these differences can be shown to have the calculated theoretical value. In the first case, the total energy change at the electrode is made up of the heat of ionisation of chlorine, minus the heat of formation of mercurous chloride, and is the same at both dilutions. If we take the temperature-coefficient of the $0.1N$ -electrode as $+0.00079$, we can at once put (per gram-equivalent):

$$U = 0.335 - 291.0.00079.$$

(Volt-faraday
at 18°)

If x is the temperature-coefficient of the N -electrode,

$$U = 0.283 - 291.x.$$

Hence:

$$0.052 = 291 (0.00079 - x)$$

$$x = +0.00061.$$

This is exactly the value found by Richards, and is confirmatory evidence in favour of his value, and against the higher figures obtained by other observers. Quite similarly, the calculated difference between the temperature-coefficients of the N - and $0.1N$ -mercuric oxide electrodes is $0.000186 \frac{\text{volt}}{\text{degree}}$, and the found value,

$$0.000176 \frac{\text{volt}}{\text{degree}}$$

In addition to this, we notice, in the same table, that, if the Planck formula be used to express the liquid potential difference $N\text{-KOH} - N\text{-KCl}$, the values for the temperature-coefficients of the electrodes $\text{Hg}|\text{HgO } N\text{-KOH}$ and $\text{Hg}|\text{HgO } N\text{-NaOH}$ are identical.

The calculated difference is only $0.00001 \frac{\text{volt}}{\text{degree}}$. If, on the other

hand, the Lewis-Sargent be used, another value is obtained for the temperature-coefficient of the electrode $\text{Hg}|\text{HgO } N\text{-KOH}$, one differing considerably from that of $\text{Hg}|\text{HgO } N\text{-NaOH}$. This good agreement between the values of the temperature-coefficients of the different electrodes justifies our assuming that the Planck formula expresses the liquid potential difference in the present cases with considerable accuracy.

Using the values of the H_2 -electrode potential in N -sodium hydroxide obtained in the previous paper, namely:

$$\begin{aligned} & -0.814 \text{ volt at } 0^\circ \\ & -0.809 \text{ volt at } 25^\circ, \end{aligned}$$

we can calculate the *E.M.F.*'s of the element $Hg|HgO \text{ } N\text{-NaOH}|H_2$ at different temperatures.

We obtain:

$$\begin{aligned} & \text{at } 0^\circ \text{ } 0.9302 \text{ volt} \\ & 18^\circ \text{ } 0.9243 \text{ ,,} \\ & 25^\circ \text{ } 0.9225 \text{ ,,} \end{aligned}$$

from which the temperature-coefficient of the cell works out at $-0.00031 \frac{\text{volt}}{\text{degree}}$. We can now calculate the heat of reaction at 18° corresponding with the equation:



We have:

$$U = A - T' \frac{dA}{dT'}.$$

$$A = 2 \times 96540 \times 0.9243 \text{ joules.}$$

$$-T' \cdot \frac{dA}{dT'} = 2 \times 96540 \times 291 \times 0.00031 \text{ joules.}$$

And

$$\begin{aligned} U &= \frac{2 \times 96540}{4.19} [0.9243 + (291 \cdot 0.00031)] \text{ calories.} \\ &= 46750 \text{ calories.} \end{aligned}$$

The thermochemical value is 46,700 calories.

Summary of Results.

(i) Combinations of the type $Hg|Hg_2Cl_2 \text{ } KCl|ROH \text{ } HgO|Hg$ are measured at 25° and 0° . The mean error varies between ± 0.00002 volt and ± 0.00011 volt.

(ii) Assuming the correctness of the Planck liquid potential formula, the following values for single potentials hold good (N -cal. at $18^\circ = +0.283$ volt):

$$Hg | HgO \text{ } N\text{-KOH} = +0.1100 - 0.00011 (t - 25^\circ)$$

$$Hg | HgO \text{ } N\text{-NaOH} = +0.1135 - 0.00011 (t - 25^\circ)$$

$$Hg | HgO \text{ } N/10\text{-NaOH} = +0.1690 + 0.00007 (t - 25^\circ).$$

The mean errors will be the same as in the corresponding combinations with calomel electrodes.

(iii) The average error of setting up is, after some days, as follows:

$$Hg | HgO \text{ } N\text{-KOH} \quad \pm 0.00019 \text{ volt}$$

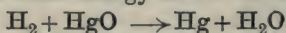
$$Hg | HgO \text{ } N\text{-NaOH} \quad \pm 0.00015 \text{ ,,}$$

$$Hg | HgO \text{ } N/10\text{-NaOH} \pm 0.00057 \text{ ,,}$$

(iv) The difference between the temperature-coefficients of the *N*- and 0.1*N*-electrodes is in close accordance with the calculated value.

(v) It follows that a standard alkaline electrode has, for the first time, been closely and accurately defined.

(vi) The change in total energy at 18° of the reaction



is calculated from electrochemical data, and shows excellent agreement with the thermochemical value.

The expenses of this work were defrayed by a grant from the Research Fund Committee of the Chemical Society, for which the authors wish to express their thanks.

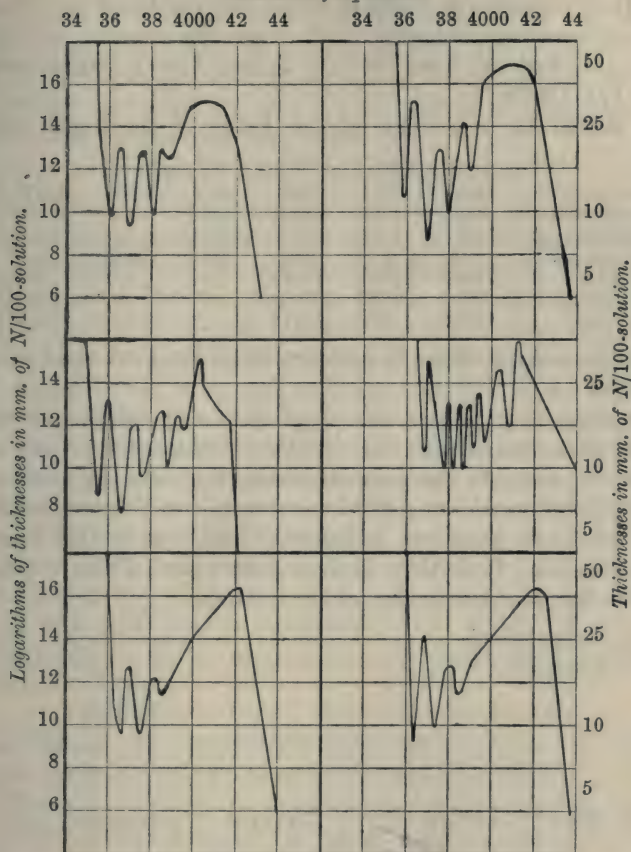
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XCI.—*The Absorption Spectra of Chlorobenzene, the Dichlorobenzenes, and the Chlorotoluenes.*

By EDWARD CHARLES CYRIL BALLY.

IN two previous papers (Baly and Collie, *Trans.*, 1905, **87**, 1332, and Baly and Ewbank, *ibid.*, 1355) the absorption spectra were described of chlorobenzene and the three dichlorobenzenes and chlorotoluenes. I am indebted to Mr. J. E. Purvis for pointing out that these substances exhibit more absorption bands than were described in the above papers. I have now repeated the examination of the seven compounds with the help of a larger and more accurate spectrograph than was available at that time, and the new results are given in Figs. 1 and 2, solutions in alcohol being used. The present results have been obtained by using as the source of light the condensed spark between cadmium electrodes, and also carbon electrodes well impregnated with molybdenum and uranium oxides. There is no doubt that whilst the small spectrograph employed in the first investigation was unsuited for the detection of the narrow absorption bands given by these compounds, the sources of light now made use of are far more adapted for the purpose than the iron arc which was originally used. At the same time, it must be pointed out that there is considerable danger in using only the cadmium spectrum, since it is possible that one or more of the absorption bands might be missed owing

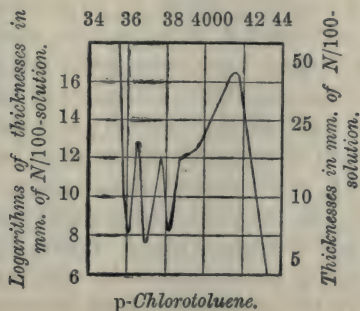
FIG. 1.
Oscillation frequencies.



Upper curves : o-Dichlorobenzene.
Middle curves : p-Dichlorobenzene.
Lower curves : o-Chlorotoluene.

m-Dichlorobenzene.
Chlorobenzene.
m-Chlorotoluene.

FIG. 2.



p-Chlorotoluene.

to their falling exactly in the position occupied by strong cadmium lines. Chlorobenzene is a case in point, for the band at $1/\lambda = 3878$ would not have been detected at all unless the uranium and molybdenum spark had also been used, for there is a very bright cadmium line at $1/\lambda = 3885$.

The oscillation frequencies of the heads of the bands are as follows:

Chlorobenzene	3682	3777	3825	3878	3920	3975	4072
<i>o</i> -Dichlorobenzene	3605	3708	3810	3880	—	—	—
<i>m</i> -Dichlorobenzene ...	3590	3698	3803	3900	—	—	—
<i>p</i> -Dichlorobenzene	3560	3660	3765	3875	3930	—	—
<i>o</i> -Chlorotoluene	3660	3758	3870	—	—	—	—
<i>m</i> -Chlorotoluene	3640	3740	3850	—	—	—	—
<i>p</i> -Chlorotoluene	3610	3705	3813	—	—	—	—

In *p*-chlorotoluene there is evidence of an incipient band at about $1/\lambda = 3900$.

It is interesting to note the progressive shift of the absorption bands towards the longer wave-lengths in passing from the ortho- through the meta- to the para-isomeride, and also the existence of one additional band in *p*-dichlorobenzene. *p*-Chlorotoluene also would appear to have one additional band, but in this case it is not so decisive. It is thus evident that none of the conclusions drawn in the previous papers are invalidated.

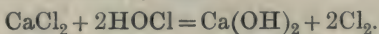
THE UNIVERSITY,
LIVERPOOL

XCII.—*The Action of Carbon Dioxide in the Bleaching Process.*

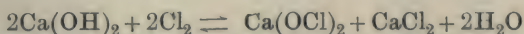
By SYDNEY HERBERT HIGGINS.

It is well known that the carbon dioxide of the air plays a part in the bleaching of vegetable fibres by hypochlorite solutions, but the nature of this part has not hitherto been thoroughly explained. A number of observations have been made which have a bearing on this matter: Williamson (*Mem. Chem. Soc.*, 1850, **2**, 234) passed chlorine into water containing calcium carbonate in suspension, when he found carbon dioxide was driven off. Dreyfuss (*Bull. Soc. chim.*, 1884, [ii], **41**, 600) showed that carbon dioxide acted on calcium chloride in the presence of hypochlorous acid to produce chlorine. Lunge and Schäppi (*Dingl. Polyt. J.*, 1889, **273**, 63) pointed out that nearly the whole of the chlorine is expelled from bleaching powder by the action of carbon dioxide. von Tiesenhoit

(*J. pr. Chem.*, 1901, [ii], **63**, 30; 1902, [ii], **65**, 512; 1906, [ii], **73**, 301) stated that the action of chlorine on alkalis is a reversible one. He explained the production of chlorine by the action of carbon dioxide on bleaching powder as being due to (1) the production of hypochlorous acid by the action of the carbon dioxide on the calcium hypochlorite, and (2) the action of this hypochlorous acid on the calcium chloride; thus:



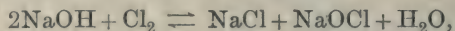
Taylor (*Trans.*, 1910, **97**, 2541) confirms von Tiesenholt's conclusion as to the reversibility of the action of chlorine on alkalis, but does not support him as regards the explanation of the production of chlorine from bleaching powder by the action of carbon dioxide. He points out that, if von Tiesenholt's view is right, hypochlorous acid cannot exist in the presence of a chloride, whereas it is known that hypochlorous acid and calcium chloride exist together in bleaching powder solution. Taylor states that the action of carbon dioxide on bleaching powder is the same as the action of any other acid, the carbon dioxide decomposing both the chloride and the hypochlorite contained in the bleaching powder. His experiments in proof of this contention, however, are not conclusive, and an explanation will be given later which better conforms with the facts. According to Taylor, when ordinary air acts on bleaching powder the free lime is removed by the action of the carbon dioxide contained in the air, and then the direction of the reversible action:



is determined; the action proceeds from right to left, the free chlorine produced being a very active bleaching agent. As is shown later, however, it is not so much the removal of the free lime from the solution of bleaching powder as the action of the carbon dioxide of the air on the solution after the free lime has been removed that increases the bleaching efficiency of the bleaching powder solution.

If the free lime be removed from the bleaching powder solution, and if an excess of calcium chloride be then added to the solution, Taylor states that the bleaching action of the resulting solution will be extremely rapid, because the two factors mentioned will both tend to make the equation given proceed from right to left. In actual bleaching, however, the present author has not found this to be the case. In support of his conclusion, Taylor mentions the experiment of breathing on to a piece of litmus paper which has been moistened with bleaching powder solution, when the rate of bleaching of the litmus is thereby greatly increased. In this case, however, the heat of the breath greatly accelerates the bleaching action, and the excess of carbon dioxide in the breath, after

precipitating the free lime, acts further on the bleaching powder solution as described later. In the reaction



Taylor states that an excess of common salt, on being added to a solution of sodium hypochlorite, causes that solution to have an increased bleaching efficiency, because it tends to make the action proceed from right to left of the equation; but the present author has shown that other neutral salts of sodium have an effect similar to that of the chloride, so that this explanation of the increased bleaching effect is untenable. Again, Taylor assumes that bleaching solutions prepared by the electrolysis of common salt solution are more active than solutions of sodium hypochlorite prepared from bleaching powder solution, whereas this has been shown (*J. Soc. Chem. Ind.*, 1911, **30**, 185) not to be the case. The explanation of the activity of old bleaching vats as being due to their exposure to air seems to have been put forward because Taylor confounded bleaching powder solutions which had been kept exposed to the air with solutions which had previously been used for bleaching (see Higgins, *loc. cit.*). The action of pure carbon dioxide on bleaching powder is attributed by Taylor entirely to the carbon dioxide, but in the action of air on bleaching powder, either in the solid state or in solution, he has no part for the carbon dioxide of the air to play except to remove the free lime from the solution, whereas it is known that the carbon dioxide of the air plays a part in actual bleaching.

The action of common salt in increasing the bleaching efficiency of hypochlorite solutions has been explained (*loc. cit.*) as being due to the increased attraction of the carbon dioxide of the air by the salt solution, and it has now been shown that this increased attraction exists in the case of lime water and calcium chloride. Taylor (*loc. cit.*) pointed out that carbon dioxide bubbled through water containing common salt, and methyl-orange caused a pink coloration, and that this coloration was produced in pure water when the carbon dioxide was at a pressure of five atmospheres. In the case of the salt solution Taylor attributed the pink colour to the liberation of hydrochloric acid from the salt by the carbon dioxide; but this explanation does not suffice for the pure water experiment. In the present author's opinion these facts are best explained as being due to the carbon dioxide being more soluble in dilute salt solutions than in pure water, although as to the state in which the carbon dioxide exists in solution no definite statement can be made. In the discussion on Taylor's paper, Senter accounted for the increased action of the carbon dioxide in the presence of common salt by the so-called "neutral salt action";

as it is shown later that neutral salts have a similar action on hypochlorite solutions, it is possible that these salts act catalytically on the hypochlorites, decreasing their stability and increasing their bleaching effect.

EXPERIMENTAL.

Absorption of Carbon Dioxide from Air by Lime Water.

The effect of adding calcium chloride to lime water on its rate of attracting carbon dioxide when exposed to air was determined in the following manner. Two equal quantities of lime water, to one of which a quantity of calcium chloride was added and the solution filtered, were exposed to air in Jena-glass beakers. After remaining for a certain time, and being periodically stirred, the solutions were filtered through weighed filter papers to collect the calcium carbonate, which had been precipitated from the solutions by the action of the carbon dioxide of the air. The filter papers were again dried and weighed. The following results were obtained:

1. 220 c.c. of lime water. A quantity of calcium chloride added to similar sample. Both solutions contained in 2-litre Jena-glass beakers.

Calcium carbonate in grams.

	After 18 hours.	After 42 hours.
Lime water alone	0.1601	0.3210
„ „ and CaCl_2	0.2311	0.3607
	After 22 hours.	
2. 100 c.c. Lime water	0.1847	
„ „ „ + 20 grams of CaCl_2 ...	0.1906	
	After 24 hours.	
3. 200 c.c. Lime water	0.2209	
„ „ „ + 15 grams of CaCl_2 ...	0.2878	
	After 22 hours.	
4. 200 c.c. Lime water	0.2035	
„ „ „ + 15 grams of CaCl_2 ...	0.2857	

Experiment 4 was a repetition of 3, but under different atmospheric conditions. In case 2 it is evident that all the lime is precipitated during the time of exposure, hence the figures obtained are practically the same for the two solutions. The figures show that the addition of calcium chloride to lime water increases the rapidity of the attraction of carbon dioxide from the atmosphere. This estimation is, of course, complicated by the slight solubility of calcium carbonate in water and its unknown solubility in calcium chloride solution. It was noticed that in the case of the pure lime water the precipitate was coarser than the other precipitate, and that it formed mostly at the surface of the solution, thus tending to shield the lime water from the further action of the air. The beaker containing the lime water and calcium chloride showed a thick deposit of calcium carbonate at the bottom, and

very little of the precipitate as a scum at the surface of the solution. It was also noticed that the pure lime water showed signs of precipitation sooner than the other solution.

Knecht has shown that the addition of calcium chloride to bleaching powder solution accelerates the bleaching action of that solution, but it has been shown (Higgins, *loc. cit.*) that under the conditions of actual bleaching this effect is very slight. The increased attraction of the carbon dioxide caused by the addition of calcium chloride, as mentioned above, causes an increased deposition of the free lime from the bleaching powder solution, and hence slightly increases the bleaching effect of that solution.

Absorption of Carbon Dioxide by Bleaching Powder Solution.

Bleaching powder solution (170 c.c. of D 1.08) was exposed to air for a number of days in a 2-litre beaker. After two days the solution had deposited 0.8 gram of calcium carbonate, and towards the end of the fifth day it was found to have lost almost all its chlorine, as it did not react with potassium iodide solution. It was noticed that the deposit of calcium carbonate was much greater than that from the same volume of lime water when exposed for a similar time (p. 861). This indicates that the calcium carbonate precipitated from the bleaching powder solution is not entirely produced from the free lime contained in that solution, but also from the other calcium salts in solution; in short, the carbon dioxide from the air, after removing the free lime, reacts with the other calcium salts. This conclusion is supported by further observations. Another sample of bleaching powder solution (400 c.c.) was now exposed to the air, and the precipitated calcium carbonate filtered off each day. After each filtration 50 c.c. of the filtrate were made up to 500 c.c., and 10 c.c. titrated with *N*/10-sodium thiosulphate (after adding potassium iodide and acidifying) to give the following results:

(a). Original solution.	10 c.c. = 16.5 c.c. thiosulphate.
(b). After 1 day's exposure.	„ = 16.4 „ „
(c). „ 2 days' „	„ = 13.7 „ „
(d). „ 3 „ „	„ = 2.6 „ „

The solution was alkaline to litmus paper after two days' exposure, but after the third day the alkalinity could not be discerned. After two days' exposure the solution was greenish, but on the third day it became colourless, and decomposed rapidly, as shown by the figures.

The bleaching effects of the solutions *a*, *b*, *c*, and *d* were now compared. Water was added in each case to make 400 c.c. of solution of the same chlorine content, and a further solution (*e*)

was obtained by adding 17 grams of pure calcium chloride to 400 c.c. of (d). Into each solution 15 grams of boiled linen were placed, and the solutions titrated at intervals as before to give the following results; 10 c.c. of solution = c.c. of thiosulphate.

	a.	b.	c.	d.	e.
Original	8.1	8.0	7.9	8.0	7.8
After $\frac{1}{2}$ hour	7.4	7.2	6.9	6.5	6.2
„ 1 „	7.3	7.0	6.7	6.1	5.9
„ 2 hours	6.9	6.7	6.3		
„ 4 „	6.7	6.5	6.1		

It is noticed that the efficiency of the bleaching liquor is only slightly increased by an exposure of two days, but after the third day this increase is very marked. Thus in the case of (d) the bleaching was performed in one hour, whereas it took four hours to bring (c) to the same point; the colours of the linen samples after bleaching confirmed the results given, yet (c) contained little or no free lime. It is therefore evident that the increased efficiency is not so much due to the removal of the free lime as to the further effect of the carbon dioxide of the air on the solution after the free lime has been eliminated. The addition of calcium chloride to the solution after the removal of the free lime as represented by (e) is seen to have no measurable effect on the bleaching efficiency, although in this case it must be remembered that (d) also contains some calcium chloride in solution, which it has retained from the original bleaching powder solution. To ascertain the effect of adding common salt to the bleaching solutions, 30 grams were added to 400 c.c. of (b) and (c) to give samples (f) and (g). Titrations were made as before.

	f.	g.
Original solution.....	7.6	7.6
After $\frac{1}{2}$ hour	6.8	6.7
„ 2 hours	6.3	6.2
„ 4 „	6.0	5.7

Comparing these results with those obtained in the case of (b) and (c) it is seen that the addition of common salt to bleaching powder solution has only a very slight effect on the bleaching efficiency, even when the free lime has been removed from that solution.

The results recorded above clearly prove that there is no advantage to be gained by leaving bleaching powder solution exposed to air in order to get rid of the free lime, as suggested by Taylor (*loc. cit.*). In another case, where a larger volume of solution was exposed and consequently proportionally less surface was under the action of the carbon dioxide of the atmosphere, a week's exposure was required in order to separate the free lime. This practice of exposing powder solution was common at one time

with bleachers because their liquors were thus made more active, but the results show that by the time the liquor is made very active it has also lost a large proportion of its chlorine.

The Effect of Neutral Sodium Salts on the Bleaching Efficiency of Sodium Hypochlorite.

It has been shown (Higgins, *loc. cit.*) that varying amounts of common salt have different effects on the bleaching efficiency of sodium hypochlorite. The effects of other neutral salts of sodium were tried, these salts being used in equivalent proportions. Solutions containing 50 grams of sodium chloride, 140 grams of crystallised sodium sulphate, and 73 grams of sodium nitrate per litre were prepared, and kept until of the same temperature. To 475 c.c. of each of these solutions and also of pure water, 25 c.c. of sodium hypochlorite solution were added, and into each solution 30.8 grams of boiled linen were placed, the solutions being tested periodically as before.

	Water.	NaCl.	Na ₂ SO ₄ .	NaNO ₃ .
Original	12.7	12.8	12.8	12.8
After 2 hours	7.9	7.1	6.9	7.3
„ 4 „	6.4	5.4	5.4	5.6

It is seen that, like common salt, other neutral salts of sodium have the effect of increasing the bleaching efficiency of sodium hypochlorite solution, and that this effect is approximately the same when equivalent proportions of the salts are used. In the above experiment the proportions of cloth, chlorine, and solution were not those used on the large scale, but were chosen to emphasise the effects of the salts.

Effect of Neutral Salts on the Bleaching Efficiency of Bleaching Powder Solution which has been Exposed to Air.

A quantity of strong bleaching powder solution was exposed to the air for four days, and the precipitate of calcium chloride filtered off. After the filtrate had remained for five days in the dark in a stoppered bottle it was used for the following experiments, which were performed to confirm previously formed conclusions.

Fifty c.c. of the solution were added to:

(a) 450 c.c. of water.

(b) 450 c.c. of the sodium chloride solution used in the previous experiment.

(c) 450 c.c. of calcium chloride solution containing 47.5 grams of the salt per litre.

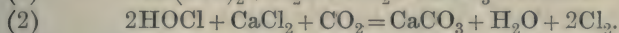
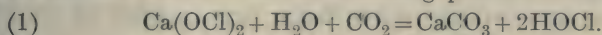
The solutions of common salt and calcium chloride contained equivalent proportions of the two salts.

30.3 Grams of boiled linen were placed in these solutions, and titrations of 25 c.c. of the solutions were made as before.

	Water.	NaCl.	CaCl ₂ .
Original.....	18.3	18.3	18.2
After 1 hour.....	11.8	11.2	11.2

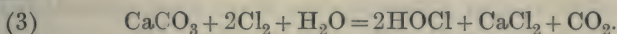
It is noticed that equivalent amounts of calcium chloride and common salt cause approximately the same increase in the efficiency of the bleaching powder solution. Moreover, this increased efficiency is only slight under the prevailing conditions, which are somewhat similar to those used in bleaching cisterns on the large scale, and is similar to the effect produced in bleaching powder solution which has not been exposed to the action of the carbon dioxide in the air (compare Taylor, *loc. cit.*).

Considering the whole of these results, it would appear that the following equations represent the action of carbon dioxide, and therefore the action of air on bleaching powder solution:

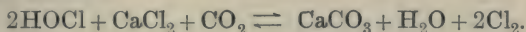


These equations explain all the facts. Thus Dreyfuss (*loc. cit.*) found that calcium chloride, carbon dioxide, and hypochlorous acid yield chlorine.

Williamson (*loc. cit.*) passed chlorine into water containing calcium carbonate in suspension, when the following reaction took place:



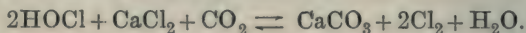
It is seen that equation (3) is the reverse of (2), so that we have a reversible action:



An excess of carbon dioxide causes the reaction to proceed from left to right, and produces pure chlorine; this is what Taylor observed on passing pure carbon dioxide through bleaching powder solution. When air containing carbon dioxide is passed through the bleaching powder solution some of the hypochlorous acid present in the solution and produced in equation (1) is swept out by the current of air, and some chlorine is produced according to equation (2). The current of air rapidly sweeps out the chlorine, and hence causes the reversible action shown to tend to proceed from left to right. On exposing bleaching powder solution to air, the carbon dioxide first precipitates the free lime and then produces hypochlorous acid and some chlorine according to the equations given. Hence a stream of air free from carbon dioxide on being led through the solution, sweeps out chlorine and hypochlorous acid. The presence of these substances accounts for the instability of the solution after exposure (p. 864). In the case of bleaching

with hypochlorite solutions in ordinary air it is therefore evident that hypochlorous acid enters into the bleaching action, and as much nascent chlorine as can be produced by the equation given.

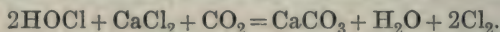
The reason that sodium chloride and calcium chloride do not assist the action of the bleaching powder to any great extent is because the carbon dioxide can only be supplied from the air at a slow rate, and this rate determines the rate of production of chlorine. In Taylor's case, where he had excess of calcium chloride and pure carbon dioxide, the chlorine would be produced at a greater rate because of the mass action:



It has been shown (p. 861) that calcium chloride assists the attraction of carbon dioxide from the air by solutions containing lime; the addition of this salt therefore assists the bleaching action of bleaching powder solution according to the equation given.

In bleaching cisterns one notices that a large amount of calcium carbonate is produced during the bleaching process; this arises from the action of the carbon dioxide of the air on the free lime of the bleaching powder solution, and also according to equations (1) and (2).

The free chlorine liberated in reaction (2) is quickly used up in oxidising the colouring matters of the textile fabrics which are immersed in the solution, and this elimination of one constituent of the reversible reaction determines the direction of this action:

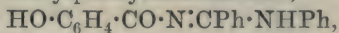


XCIII.—*The Condensation of Acetyl Chloride and Salicylamide.*

By ARTHUR WALSH TITHERLEY and WILLIAM LONGTON HICKS.

It has already been shown by McConnan and Titherley (Trans., 1906, **89**, 1334) that salicylamide reacts with acetyl chloride at its boiling point, yielding a solid chloro-derivative which, on treatment with water, decomposes, with formation of hydrogen chloride and *N*-acetylsalicylamide in 85 per cent. yield, and it was supposed on analytical grounds that the chloro-derivative was identical with the compound obtained by the action of hydrogen chloride on *N*-acetylsalicylamide. The action of acetyl chloride on salicylamide has since been studied under a variety of conditions, and it has been shown that the two products containing chlorine are not identical,

since they behave differently with aniline. The solid obtained by the action of hydrogen chloride on *N*-acetylsalicylamide is evidently a simple hydrochloride, because it yields *N*-acetylsalicylamide with aniline, but the product obtained from acetyl chloride and salicylamide on treatment in presence of ether with aniline yields a beautiful yellow, crystalline solid, which has been proved to be salicylphenylacetamidine, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}:\text{CMe}\cdot\text{NHPh}$. It was therefore at first assumed that the chloro-compound had the constitution $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}:\text{CMeCl}$, but parallel experiments on the action of aniline on 2-phenyl-1:3-benzoxazine-4-one (Titherley, *Trans.*, 1910, **97**, 204), or its hydrochloride, in which a similar yellow derivative, salicylphenylbenzamidine,

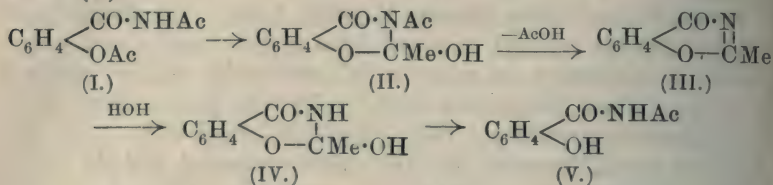


is formed, makes it probable that the solid white substance obtained from acetyl chloride and salicylamide is the hydrochloride of 2-methyl-1:3-benzoxazine-4-one, $\text{C}_6\text{H}_4\begin{matrix} \text{CO}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{O}-\text{C}\cdot\text{CH}_3 \end{matrix}$, which with aniline would be expected to behave like the phenyl derivative.

All attempts, however, to isolate this cyclic compound from the reaction product have failed, and, further, attempts to synthesise it by methods analogous to those (*loc. cit.*) which have succeeded with 2-phenyl-1:3-benzoxazine-4-one have proved fruitless, probably because the former compound is much less stable than the latter, and is decomposed during the treatment with alkali. It is hoped by suitable modification of this treatment to isolate the compound.

In the action between acetyl chloride and salicylamide it has been found that although an immediate change takes place in the cold in which salicylamide hydrochloride is precipitated, no *O*-acetylsalicylamide is produced, and it is probable that the latter undergoes immediate rearrangement to its *N*-acetyl isomeride, and it is only by slow further action of hot acetyl chloride in excess that dehydration occurs, producing the supposed 2-methyl-1:3-benzoxazine-4-one hydrochloride. By long continued boiling a small quantity of *O*-*N*-diacetylsalicylamide (I) is produced. This compound, which can be best obtained from *N*-acetylsalicylamide and acetic anhydride in the presence of pyridine, is remarkable (1) by being readily soluble in water, and (2) by being slowly hydrolysed by atmospheric moisture, yielding *N*-acetylsalicylamide and acetic acid. These properties, which are unlike those of any other acylsalicylamides investigated by the authors, suggest that diacetylsalicylamide readily assumes the tautomeric constitution (II), which would be favourable to loss of acetic acid, yielding the unsaturated compound (III); this, then, in the presence of acetic acid or water, like its phenyl analogue, would give the unstable

hydroxy-derivative (IV), which at once passes into *N*-acetylsalicylamide (V):



EXPERIMENTAL.

A mixture of 25 grams of salicylamide and 50 grams of acetyl chloride was heated at 60° in a reflux apparatus for twenty-four hours. The granular solid so obtained was collected rapidly, washed with light petroleum and pure ether, suspended in 100 c.c. of ether, and treated with 40 grams of pure aniline. An immediate yellow colour developed, and the mixture was heated to the boiling point for three hours. After removing the insoluble aniline hydrochloride (25.5 grams), which contained about 2.5 grams of *N*-acetylsalicylamide, the yellow ethereal filtrate was kept in a cold place for twenty-four hours, when salicylphenylacetamidine was deposited in massive, transparent, yellow crystals (13 grams), melting at 70°. The ethereal mother liquor on evaporation left a yellow syrup containing salicylamide (6 grams), and a solid substance, which was identified as diphenylacetamidine (16 grams), and remained insoluble after digestion with aqueous alkali. It was obtained pure in fine needles after recrystallisation from 85 per cent. aqueous methyl alcohol, and melted at 134°. (Found, N=13.44. Calc., N=13.33 per cent.)

The diphenylacetamidine was found to be produced by the secondary action of aniline on salicylphenylacetamidine in a similar manner to that (Titherley, *loc. cit.*) by which diphenylbenzamidine is produced from salicylphenylbenzamidine. The reaction between acetyl chloride and salicylamide was also examined under many other conditions at temperatures between 15° and 110°, both with and without benzene as a solvent. In the cold, only salicylamide and *N*-acetylsalicylamide hydrochlorides were formed, which yielded no salicylphenylacetamidine on treatment with aniline. At high temperatures darkening occurred with general decomposition, and the best yield of salicylphenylacetamidine was obtained under the conditions described above.

Salicylphenylacetamidine,

When obtained by the above method the compound may be purified by recrystallisation from hot light petroleum, from which it separates in small, pale yellow needles, melting at 77° :

0.2152 gave 19.35 c.c. N_2 at 12° and 775 mm. $\text{N}=10.87$.

$\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{N}=11.02$ per cent.

The compound is very soluble in benzene and readily in alcohol, but less so in ether, and very sparingly soluble in cold light petroleum. It gives a deep brownish-red colour in acetone solution with ferric chloride, and dissolves in aqueous sodium hydroxide, giving a pale yellow solution, from which it may be precipitated by careful neutralisation with dilute acetic acid. With mineral acids the substance is rapidly decomposed with loss of aniline and formation of *N*-acetylsalicylamide, which is obtained as a white precipitate, melting at 148° . In these properties the substance is similar to salicylphenylbenzamidine, but it differs from the latter in slowly decomposing in the air at the ordinary temperature. After being kept for about twelve months, the yellow crystals fall to a white, opaque solid of indefinite melting point; on now digesting with aqueous ammonia about one-third remains insoluble, and, after recrystallisation from aqueous methyl alcohol, melts at 132 – 133° (diphenylacetamidine), whilst the yellow filtrate, on acidification with dilute acid, gives a mixture of salicylamide and *N*-acetylsalicylamide, which were incompletely separated by digestion with aqueous sodium hydrogen carbonate (the former being scarcely affected and the latter dissolving) and repeated recrystallisation. It is therefore evident that atmospheric moisture slowly decomposes salicylphenylacetamidine, giving diphenylacetamidine, salicylamide, and *N*-acetylsalicylamide, and it is probable that the cyclic compound $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CMe} \end{smallmatrix}$ is an intermediate product in the change.

O-N-Diacetylsalicylamide, $\text{AcO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHAc}$.

This compound is found in small quantities in the filtrate from the insoluble hydrochloride obtained after long heating of salicylamide with acetyl chloride; and was isolated in the unsuccessful attempts to prepare 2-methyl-1:3-benzoxazine-4-one by using sodium acetate as catalyst. Fourteen grams of salicylamide, 25 grams of acetyl chloride, and 8 grams of anhydrous sodium acetate were heated at 60° for two hours, and then benzene was added. The filtrate was first shaken with water to remove acetyl chloride, and

then with sodium hydrogen carbonate solution, and the dried benzene solution was then evaporated. A clear syrup remained (about 0.4 gram), which was dissolved in hot light petroleum; on cooling slowly, beautiful large prisms of *O-N*-diacetylsalicylamide separated, melting at 67° , which gave no ferric chloride coloration in acetone solution.

Preparation from N-Acetylsalicylamide.—A mixture of 20.5 grams of *N*-acetylsalicylamide and 50 grams of pure pyridine was treated gradually at 0° with 14 grams of acetic anhydride, kept at 0° for one and a-half hours, and finally at room temperature for half an hour. The product was then cooled to 0° , treated with 200 c.c. of ether, and gradually with an ice-cold mixture of 100 c.c. of saturated ammonium sulphate solution and 80 grams of sulphuric acid, with continual stirring. After drying the ethereal solution and distilling off the ether, a yellow oil remained, which contained much acetic acid, and on keeping in a desiccator over potassium hydroxide deposited *O-N*-diacetylsalicylamide in rectangular prisms. The yield, after draining, was 18 grams, and the product melted at 67° . It was freed from the last traces of acetic acid by dissolving in 150 c.c. of ether, and shaking with potassium carbonate and a little water. The ethereal solution on evaporation deposited massive, inch-long, transparent prisms, melting at $67-68^{\circ}$:

(1) 0.3238, by Kjeldahl's method, required 15.5 c.c. *N*/10-HCl.
N = 6.70.

(2) 0.2521 gave 14.3 c.c. N_2 at 19° and 760 mm. N = 6.50.

$C_{11}H_{11}O_4N$ requires N = 6.33 per cent.

O-N-Diacetylsalicylamide is readily soluble in alcohol, ether, acetone, benzene, chloroform, ethyl acetate, pyridine, or acetic acid, and sparingly so in cold light petroleum. From the latter solvent, when hot, it tends to separate as an oil unless the solution is very slowly cooled. It is fairly easily soluble in cold water, and crystallises out unchanged on evaporating the solution immediately under diminished pressure, but on long keeping in aqueous solution it is decomposed with the formation of *N*-acetylsalicylamide, which separates out. Ammonia effects the same hydrolytic decomposition instantly, with the formation of a pale yellow solution of the ammonium salt of *N*-acetylsalicylamide. The aqueous solution gives no colour with ferric chloride, except on keeping, when the purple coloration due to *N*-acetylsalicylamide develops.

O-N-Diacetylsalicylamide is very slowly decomposed by atmospheric moisture; the large, transparent crystals gradually become opaque and moist, owing to the formation of *N*-acetylsalicylamide and acetic acid. A specimen which had been kept in an ordinary

stoppered bottle for twelve months was found to have undergone this decomposition to the extent of about 30 per cent. As this change suggests the intermediate formation of 2-methyl-1:3-benz-oxazine-4-one, attempts were made to isolate this compound by eliminating acetic acid from the diacetyl derivative by various means, but without success. Further investigations are proceeding with the object of isolating this unsaturated cyclic compound.

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XCIV.—*The Volume of a Solute in Solution. Part II.
The Influences of Molecular Association, Solvate
Formation and Ionisation.*

By DAN TYRER.

IN a previous communication (Trans., 1910, **97**, 2620) it was shown that the volume of a solute in a solvent is constant, independent of the concentration, and differing but slightly from solvent to solvent.

With this rule established, it becomes possible to study systematically the influences of molecular association, solvate formation, and ionisation on the specific volume of the solute in solution. These are points which have been rather neglected by previous investigators, whose work has been almost wholly confined to aqueous solutions where all three factors may come into play. Traube (*Annalen*, 1896, **290**, 43), for example, studied a large number of aqueous solutions, and although he eliminated the influence of ionisation by considering non-electrolytes, the other two factors played an unknown part, vitiating to some extent the accuracy of his conclusions. It is impossible to generalise with safety from results for aqueous solutions, unless the influences of these secondary factors are properly understood.

By taking, in the first place, cases in which the solute polymerises in solution and does not combine with the solvent, we can determine the influence of molecular association on the specific solution volume of the solute. In the second place, by taking cases where the solute is known to combine with the solvent, we can study the effect of solvate formation. The influence of ionisation can be determined by a study of aqueous solutions of electrolytes and by a comparison of the behaviour of these with that of non-electrolytes. The method

of working consists simply in determining the specific volumes of solutions of known concentrations, the specific volume of the dissolved substance being then calculated by means of the formula

$$v = \frac{(100 + A)S_1 - 100S_0}{A},$$

where v is the specific volume of the solute in solution, A is the percentage concentration of the solution (grams of solute per 100 of solvent), S_1 the specific volume of the solution, and S_0 the specific volume of the pure solvent at the same temperature.

Measurements were made by means of a quartz pycnometer.

The specific volume determinations were made to within a mean error not greater than one unit in the fifth place. All the measurements were made at the constant temperature of 12.87° , obtained in a bath of running water, the temperature of which could be controlled to within 0.005° . The details of the working are described in the previous paper (*loc. cit.*).

All the substances used were carefully purified; as a rule, Kahlbaum's chemicals were further purified by redistillation or crystallisation.

The Influence of Molecular Association.

In the following tables are given the specific volumes, v , of some hydroxyl compounds dissolved in normal solvents. In all cases the solute exists in solution as complex molecules, the complexity of which increases with the concentration (see Beckmann, *Zeitsch. physikal. Chem.*, 1882, **2**, 715; Auwers and Orton, *ibid.*, 1896, **21**, 337).

The results are for the constant temperature of 12.87° .

Phenol in Toluene ($S_0 = 1.14636$).

A .	S_1 .	v .
2.136	1.14152	0.915
4.446	1.13656	0.916
10.916	1.12376	0.917
23.042	1.10326	0.916
40.428	1.08047	0.917

Phenol in Chloroform ($S_0 = 0.66587$).

A .	S_1 .	v .
4.029	0.67562	0.917
7.450	0.68324	0.916
13.637	0.69591	0.916
28.251	0.72106	0.916

Benzoic Acid in Benzene ($S_0 = 1.12819$).

A .	S_1 .	v .
2.158	1.12251	0.859
4.528	1.11649	0.858
7.279	1.10992	0.859

Benzoic Acid in Chloroform.

A .	S_1 .	v .
1.555	0.66861	0.845
3.659	0.67227	0.847
9.207	0.68105	0.846

Monochloroacetic Acid in Benzene.

A .	S_1 .	v .
4.129	1.11216	0.724
9.176	1.09405	0.722
12.183	1.08395	0.721

Monochloroacetic Acid in Toluene.

A .	S_1 .	v .
2.615	1.13530	0.713
8.852	1.11099	0.712
12.359	1.09851	0.711

o-Cresol in Benzene.

A.	S_1 .	v.
3·757	1·12164	0·947
5·456	1·11886	0·948
12·418	1·10810	0·946
28·659	1·08772	0·947

o-Cresol in Nitrobenzene ($S_0=0·82600$).

A.	S_1 .	v.
3·178	0·82985	0·951
10·552	0·83808	0·952
19·361	0·84644	0·952

Acetic Acid in Benzene.

A.	S_1 .	v.
4·220	1·12270	0·992
8·715	1·11704	0·989
24·060	1·10006	0·983
30·548	1·09368	0·981

Acetic Acid in Toluene.

A.	S_1 .	v.
3·111	1·14133	0·979
7·548	1·13456	0·978
13·792	1·12587	0·976
16·862	1·12182	0·976

Methyl Alcohol in Benzene ($S_0=1·12842$).

A.	S_1 .	v.
1·900	1·13075	1·253
7·883	1·13748	1·252
16·375	1·14574	1·252
24·426	1·15252	1·251
27·270	1·15466	1·251
62·162	1·17546	1·251

o-Nitrophenol in Benzene.

A.	S_1 .	v.
3·127	1·11691	0·755
7·089	1·10354	0·755
12·916	1·08546	0·754
33·521	1·03418	0·754

It will be seen from the above tables that the specific volume of the solute in solution is, in all cases, with the exception of acetic acid in benzene, independent of the concentration. Now in all the above cases the solute is associated in solution, and the degree of association increases with increase of concentration. For example, Beckmann (*loc. cit.*) found that phenol in benzene at a concentration of 0·34 per cent. has a molecular weight of 143, and at a concentration of 2·5 per cent. the molecular weight is 161, the normal molecular weight being 94.

It may be concluded, therefore, from these experiments that the specific volume of a solute in solution is independent of its degree of association.

It will be noticed that in those cases given above where determinations have been made for a given solute in two different solvents, that the specific volume of the solute is not the same in both. The slight difference is merely the normal effect of the solvent which was studied in the previous paper (*loc. cit.*). In regard to the exceptional case of acetic acid and benzene, this might be explained (as will presently be seen) by supposing that the acetic acid combines to some extent with the benzene, although there is no other evidence to support this.

The Influence of Solvate Formation.

There appears to be few cases where there is certain evidence that the solute (which must not be ionised) combines with the solvent when dissolved. From what has just been established, it follows that it does not matter whether the solute is associated or not.

One case of this class was mentioned in the previous paper, namely, that of triphenylmethane in benzene, and it was found that the specific volume of the solute in this solution is not sensibly different from the values in other normal solvents. In this case evidently, solvate formation does not influence the apparent volume of the solute. This is supported by a few other cases given below, but, as will be seen, the rule is not general.

Calcium Chloride in Methyl Alcohol
($S_0 = 1.25078$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
1.006	1.23642	-0.19
2.114	1.22192	-0.143
6.877	1.16564	-0.072
9.348	1.13992	-0.046

Calcium Chloride in Ethyl Alcohol
($S_0 = 1.25651$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
1.729	1.23446	0.120
3.815	1.21288	0.143
4.842	1.20272	0.149

Calcium chloride combines with methyl alcohol, forming a compound of the formula $\text{CaCl}_2 \cdot 4\text{CH}_3\text{O}$, and a similar compound with ethyl alcohol. There can be little doubt that these compounds exist also in solution, and that the amount formed will decrease with the concentration. This change is shown by a constant increase in the value of the specific solution volume. In the case of methyl alcohol, the volume of the solution is less than the volume of methyl alcohol it contains.

m-Dinitrobenzene in Toluene Solutions of Naphthalene.

m-Dinitrobenzene crystallises with naphthalene like picric acid. As picric acid itself is too sparingly soluble, it was considered of interest to determine the specific volume of *m*-dinitrobenzene in solutions of naphthalene in toluene, and to compare them with values found in other solvents.

Solution A.

1.259 per cent. of naphthalene
($S_0 = 1.14396$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
2.637	1.13156	0.661
4.563	1.12296	0.663
7.846	1.10905	0.664
11.903	1.09304	0.665

Solution B.

5.334 per cent. of naphthalene
($S_0 = 1.13678$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
2.618	1.12482	0.667
5.651	1.11161	0.666
9.961	1.09411	0.666

Solution C.

7.825 per cent. of naphthalene
($S_0 = 1.13265$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
1.060	1.12778	0.668
3.306	1.11772	0.666

Solution D.

25.449 per cent. of naphthalene
($S_0 = 1.10852$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
3.250	1.09455	0.665
23.051	1.02633	0.669

In Pure Toluene.

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
3.123	1.13153	0.660
10.478	1.10051	0.663

It is clear from the above that the formation of a compound of naphthalene with *m*-dinitrobenzene has but little effect on the apparent specific solution-volume of the latter.

Trinitrotoluene in Benzene Solutions of Naphthalene.

Like dinitrobenzene, trinitrotoluene also crystallises with naphthalene from a mixed solution of the two. The specific volumes of trinitrotoluene have been determined in two different solutions of naphthalene in benzene, and for the sake of comparison in pure benzene and also in chloroform, the latter being also used in case the solute combined with benzene as well as with the naphthalene.

<i>Solution A.</i>			<i>Solution B.</i>		
2·423 per cent. of naphthalene ($S_0=1\cdot12428$).			9·642 per cent. of naphthalene ($S_0=1\cdot11352$).		
<i>A.</i>	S_1 .	<i>v.</i>	<i>A.</i>	S_1 .	<i>v.</i>
2·507	1·11219	0·630	5·289	1·08922	0·630
6·795	1·09296	0·632	6·262	1·08502	0·631
14·856	1·06062	0·632	10·701	1·06690	0·631

<i>Trinitrotoluene in Pure Benzene.</i>			<i>Trinitrotoluene in Chloroform.</i>		
<i>A.</i>	S_1 .	<i>v.</i>	<i>A.</i>	S_1 .	<i>v.</i>
4·211	1·10818	0·633	1·628	0·66516	0·622
7·833	1·09219	0·633	2·622	0·66468	0·619
12·840	1·07185	0·633	3·202	0·66454	0·623
15·462	1·06184	0·633			

In this case, as in the previous example, the apparent volume of the solute is unaltered by its combination with a portion of the solvent.

Acetic Acid in Aniline ($S_0=0\cdot97295$).

<i>A.</i>	S_1 .	<i>v.</i>
4·015	0·96986	0·893
6·119	0·96824	0·891
11·293	0·96401	0·885
14·356	0·96168	0·814

If these values of *v* be compared with those found in toluene, it will be seen that they are considerably less; hence, in this case, combination with the solvent causes a marked contraction in volume.

Benzoic Acid in Aniline.

<i>A.</i>	S_1 .	<i>v.</i>
1·810	0·97046	0·832
5·603	0·96543	0·832
9·885	0·96008	0·830
13·854	0·95543	0·829

On comparing these values with those found in benzene, it will be seen that they are decidedly lower, but that the difference is not so well marked as in the previous case.

Results Calculated from Measurements of Other Observers.

A few cases have been selected from work of previous investigators which have a bearing on the present question. They are all in aqueous solution, from which the solute crystallises with water of crystallisation. It is therefore tolerably certain that these substances form hydrates in aqueous solution, and any appreciable deviation from constancy of the specific volumes of these substances, as the concentration varies, can only be attributed, from what has so far been established, to the influence of solvate formation, or, rather, to the variation in the degree of hydration. A few of the cases below are weak electrolytes, but the amount of ionisation is negligibly small.

Dextrose. ¹ $C_6H_{12}O_6 + H_2O$.		Lactose. ¹ $C_{12}H_{22}O_{11} + H_2O$.		Maltose. ¹ $C_{12}H_{22}O_{11} + H_2O$.		Gallotannic Acid. ² $C_{14}H_{10}O_9 + 2H_2O$.		Citric Acid. ² $C_6H_8O_7 + H_2O$.	
A.	v.	A.	v.	A.	v.	A.	v.	A.	v.
5.19	0.614	2.52	0.608	8.11	0.599	4	0.562	9.14	0.588
10.09	0.624	10.44	0.624	16.98	0.597	8	0.564	18.29	0.593
15.85	0.626	21.97	0.628	28.25	0.611	10	0.566	27.43	0.596
32.35	0.627	—	—	—	—	18	0.574	40.71	0.605

¹ Kannonikoff, *J. pr. Chem.*, 1894, [ii], 49, 170.

² See Traube, *Annalen*, 1896, 290, 66, 92.

It will be noticed that there is a gradual increase in the specific volume of the solute with increase of concentration. This can only mean that in these cases hydration takes place, the degree of which decreases as the concentration increases. This increase of the solution volume with increase of concentration is the behaviour of practically all non-electrolytes in aqueous solution. The above cases were selected for illustration simply because hydrates of these substances actually exist. We have seen that the rule for normal substances is the independence of the specific solution volume on the concentration, and, further, that this rule is equally true for cases where the solute is polymerised in solution. But as has just been stated, in aqueous solution very few substances (non-electrolytes) obey this rule. The well known case of sugar in water is only in approximate agreement with the rule. This well-marked difference between the behaviour of aqueous solutions and solutions in normal solvents can only be satisfactorily explained on the supposition that in practically all aqueous solutions of non-electrolytes, hydration to some extent takes place. It must be pointed out that non-electrolytes which are soluble even only to a small extent in water, are almost wholly substances which, in the pure state, are associated, such as the hydroxyl compounds, amino-compounds, and the lower ketones. It is not, then, very surprising to find evidence that these substances form solvates in their solutions in associated

solvents. That the behaviour is true for other solvents than water is shown by the following few examples.

<i>Phenol in Ethyl Alcohol.</i>			<i>o-Nitrophenol in Ethyl Alcohol.</i>			<i>Glycerol in Ethyl Alcohol.</i>		
<i>A.</i>	<i>S₁.</i>	<i>v.</i>	<i>A.</i>	<i>S₁.</i>	<i>v.</i>	<i>A.</i>	<i>S₁.</i>	<i>v.</i>
3.784	1.23993	0.875	2.491	1.24235	0.674	3.261	1.23975	0.726
6.062	1.23214	0.876	6.920	1.22095	0.707	4.829	1.23231	0.731
9.856	1.22012	0.879	12.349	1.19643	0.709	13.575	1.19442	0.737
17.159	1.19931	0.882	12.626	1.19531	0.711	36.471	1.12085	0.749
25.838	1.17810	0.885	—	—	—	—	—	—

It will be noticed that the values of *v* increase in a regular manner as the concentration increases, and if these values in the cases of phenol and nitrophenol be compared with their values in normal solvents, it will be seen that they are considerably lower. There can be little doubt that in these solutions solvates are formed.

Summarising the data given above, the following conclusion may be drawn in regard to influence of solvate formation on the volume of the solute in solution. When a dissolved substance forms an unstable compound or solvate with the solvent, the specific volume of the former is not generally constant, but increases as the concentration of the solution increases. This is, however, not always the case, as has been shown. The variation of the specific solution volume can, however, only conceivably take place when solvates are formed. The increase with increase of concentration runs parallel with the decrease of the amount of solvate formed. It does not, however, necessarily happen, although it probably holds in the majority of cases, that the amount of solvate formed decreases with increase of the concentration. There is the well known case of alcohol and water, which gives a minimum value for the specific volume of the alcohol in solution. In such a case, there exists a solvate with an unusually great stability, which is the principal product of the reaction over a wide range of concentration. In any case, whether a decrease or increase of the solution volume of a solute (non-electrolyte) takes place when the concentration increases, its variation may be regarded as a true criterion of solvate formation.

The Influence of Ionisation.

A large amount of experimental data has been accumulated on densities and specific volumes of aqueous solutions of electrolytes. Yet no generalisations of importance have resulted. This is due, no doubt, to the complexity of factors which come into play. We have to deal with the following possibilities, all of which may vary with the concentration :

- (1) Ionisation.
- (2) Association of molecules of solute.
- (3) Association of molecules of solvent.
- (4) Hydration of undissociated solute.
- (5) Hydration of ions.

We have seen that molecular association does not affect the volume of the solute in solution, and therefore factor (2), if it exists, can be neglected. In regard to factor (3), we have seen that when two substances form a homogeneous mixture, the specific volume of the one is constant, whether it exists in the mixture in the form of simple molecules, or in the form of associated molecules. It clearly cannot matter which of the two substances is associated, or whether both are associated in the mixture. The rule will hold in any case. We can, therefore, neglect factor (3).

It has been found that in almost all cases the volume of the solute in solution in the cases of electrolytes decreases as the concentration decreases. There are very few exceptions to this rule. Ammonia, hydrobromic acid, and hydriodic acid give fairly constant values over moderately wide ranges of temperature (Carius and Topsøe, *Zeitsch. anal. Chem.*, 1869, **8**, 279). This change persists also even at extremely dilute solutions. The following example, taken from measurements of Kohlrausch (*Ann. Phys. Chem.*, 1895, [iii], **56**, 185) and Mendeléeff (*Zeitsch. physikal. Chem.*, 1887, **1**, 273), is typical.

Sulphuric Acid.

Concentration per cent.	Molecular volume of H_2SO_4 in solution at 6° (Kohlrausch).	Concentration per cent.	Molecular volume of H_2SO_4 in solution at 0° (Mendeléeff).
0.002	5.9	1.34	25.7
0.01	7.71	5.16	29.8
0.05	10.75	17.88	33.3
0.1	12.03	30.34	36.6
1.0	15.54	52.13	41.4
5.0	17.57	83.05	46.3

The volume of an electrolyte in solution shows no tendency to assume a constant value, but goes on decreasing as the dilution increases, and in many cases becomes negative. In such cases, the volume of the solution is less than the volume of water it contains. Obviously a contraction or condensation of the water by the electrolyte has taken place. Cameron and Robinson (*J. Physical Chem.*, 1910, **14**, 1) have measured the amount of this condensation for a few cases, but no regularities have been discovered. Negative solution volumes at small concentrations have been observed in the following cases: sodium hydroxide (Kohlrausch, *Ann. Phys. Chem.*,

1879, [iii], 6, 1); sodium sulphide (Boch, *ibid.*, 1887, [iii], 30, 638); magnesium sulphate (Kohlrausch, *ibid.*, 1895, [iii], 56, 185). There can be no doubt that in many other cases also, the solution volumes would assume negative values at sufficiently great dilution. But this is by no means a general property, for even with some strong electrolytes in very dilute solution, the solution volume of the solute has a comparatively large positive value. For example, sodium chloride at a concentration of 0.3 per cent. has a molecular volume of 17.8, and at 20 per cent. its molecular volume is 20.4 (Schütt, *Zeitsch. physikal. Chem.*, 1890, 5, 536). In this case the variation with concentration is very small. It is clear, then, that a complexity of factors comes into play. The simple effect of dissociation fails to explain why the ions assume a negative value for the specific solution volumes. There is, indeed, no relation whatever between the degree of ionisation and the solution volume. Obviously, condensation of water by the ions takes place: yet this does not necessarily mean that the ions are hydrated, for it may simply mean that the water molecules are attracted into closer proximity around each ion, and in this connexion it is interesting to observe that the charged particles in colloidal solutions condense or contract the solvent in a similar manner. The formation of a hydrate in the case of a colloidal solution would be, of course, impossible, and it would seem to suggest that the condensation of the solvent is a property of charged particles of the solute. This explanation does not, however, cover all the facts, for it would follow that particles carrying the same charge would produce equal contractions, which is not the case. The simple effect of ionisation, then, fails to explain all the facts, and since in extremely dilute solutions, when almost all the salt is ionised, the decrease of the volume of the solute in solution with decrease of the concentration still persists, we can only conclude that the ions become hydrated, the degree of hydration varying with the concentration, and depending also on the nature of the ion.

In strong solutions, as in the case of non-electrolytes, the volume of the solute in solution varies with the concentration, and there can be little doubt, therefore, that hydrates of varying complexity are formed.

Summary.

The results of this work may be summarised as follows:

- (1) In solutions in which no chemical changes of any kind occur, the specific volume of the solute is constant, independent of the concentration. Its value varies slightly for different solvents.
- (2) Molecular association of the solute in solution is without

influence on the apparent volume of the solute. The behaviour is the same as if the molecules were normal.

(3) Solvate formation, that is, combination of the solvent and solute, generally causes a contraction in the apparent volume of the solute, and, further, the volume of the solute in solution generally decreases with decrease of concentration. But in some of the cases investigated, the formation of a solvate appears to be without influence on the solution volume of the solute.

(4) Variation of the specific solution volume of a non-electrolyte with variation of the concentration may be regarded as a true criterion of solvate formation. From this it follows that in almost all cases of aqueous solutions of non-electrolytes hydrates are formed.

(5) With aqueous solutions of electrolytes it is probable that in strong solutions the undissociated molecules are hydrated, and in dilute solutions the ions are also probably hydrated.

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XCV.—*Molecular Association and its Relationship to Electrolytic Dissociation. The Molecular Complexity of Halogen-containing Compounds.*

By WILLIAM ERNEST STEPHEN TURNER.

DURING recent years, largely as the outcome of the study of molecular compounds, theories of valency have undergone considerable changes. The former views, which assigned a definite valency to a particular element, and saw in the combination between molecules, alike or different, the action only of a modified form of valency possessed by the molecule as a whole, have been substituted by others which seek to assign to each separate element, not only a definite power of combination within a distinct molecular unit, but a certain residual, latent, or changing valency. They assert, in other words, that molecular compounds are not due to the valency of each molecule, as a whole, but to the presence within them of such elements as are possessed of latent valencies.

These views have been applied, not only to cases of definite compound formation, but to assist also in the classification of physical phenomena, especially in connexion with the problems in which either electrolytic dissociation or molecular association is

concerned. As regards the latter, Guye, for example, has suggested that the association of certain organic liquids containing unsaturated nitrogen or oxygen is due to chemical forces (Guye and Baud, *Compt. rend.*, 1901, **132**, 1555). Abegg, whose theory of valency is generally recognised as a valuable means of classification, took the view that association, either of similar or dissimilar molecules,* could be attributed to the latent or contra-valencies of elements, as distinct from the so-called normal valencies. After showing that the number of these contra-valencies possessed by an element increases as we pass from left to right in the Periodic table, Abegg states (*Zeitsch. anorg. Chem.*, 1904, **39**, 330): "... wir können nun weiter alle assoziierten Molekeln als durch chemische zwischen Atomen wirkende Kräfte verbunden erklären, sofern es gelingt nachzuweisen, dass in ihren Komponenten Elemente vorhanden sind, deren Maximalvalenz in nicht assoziierter Form noch nicht ausgenutzt ist." And, again, "Je weiter ein solches Element im periodischen System nach recht steht, um so grösser wird seine Fähigkeit, sich mit sich selbst oder anderen Atomen . . . zusammenzulagern. . . ."

Then are mentioned as illustrations certain oxides, organic hydroxylic compounds, and, further, all of them salts or electrolytes, a number of chlorine compounds.

We are thus led to expect the occurrence of molecular association among the halogen compounds to at least the same extent as among those of oxygen. A consideration of certain of the illustrations leads to this position. And, at any rate, recent interpretations of the function of latent valencies make it clear that the deduction has good foundation. Thus, according to the later theory of Friend (*Trans.*, 1908, **93**, 260; "Theory of Valency," 1909, p. 100), the fact that *o*-chlorophenol is non-associated, whereas both the *m*- and *p*-compounds undergo association, is explained on the supposition that the latent valencies of the oxygen atom are neutralised by those of the chlorine atom. This suggestion, which has been repeated recently by Thole (*Trans.*, 1910, **97**, 2603), appears to be entirely consistent with the statement of the theories, both of Abegg and of Friend. The view involves the assumption, however, that these forces acting within the molecule to restrain association are just as capable, when either of the conjugate groups is removed, of external activity to bring about association. That is to say, chloro- or iodo-benzene should be capable of association.

* The present communication is intended to deal only with association of similar molecules. The author hopes in another paper to make reference to association of dissimilar molecules.

It was the object of this investigation to test, in the first place, how far the theory that molecular association is due to the latent valencies of individual elements within the molecule is capable of experimental realisation. At first, the research was confined to carbon compounds containing halogens, but it was soon expanded into a review of all types of compounds containing these elements.

Of the various classes of substances dealt with, the most important is that of salts. The metallic compounds of the halogens have received more thorough investigation than any other salts, whether at high temperature, as vapour, or at lower temperatures, in solution. All the vapour density determinations, as, for example, those of Deville and Troost (*Compt. rend.*, 1857, **45**, 821; *Ann. Chim. Phys.*, 1860, [iii], **58**, 557), Friedel and Crafts (*Compt. rend.*, 1888, **106**, 1764), Nilson and Pettersson (*Zeitsch. physikal. Chem.*, 1887, **1**, 459; 1889, **4**, 206), V. Meyer and C. Meyer (*Ber.*, 1879, **12**, 609, 1112, 1185, and 1292), and Biltz and V. Meyer (*Ber.*, 1889, **22**, 725), on the halogen compounds of aluminium, and on ferric and cuprous chlorides were undertaken in order to test whether a simple or a double formula should be assigned. Less attention was paid to the fact that molecular association varied with the temperature. This communication emphasises the fact that molecular association, like electrolytic dissociation, is progressive, and varies both with concentration and temperature. On this view, it is best to assign the simple or unimolecular formulæ to most salts, just as fractional values are not assigned to a salt from the molecular-weight results obtained in aqueous solution. We should, in fact, adopt for general use the limiting value of the molecular formula, not simply because of the measurements quoted on p. 900, but because any other formula is dependent on the circumstances of the measurement, on the temperature, on the nature of the medium, and on the concentration. Only cuprous chloride appears to have a strong claim to the double formula, since its molecules resist dissociation, even at 1600°. In certain other cases it is known that dissociation into simple molecules occurs on rise of temperature. The substances still found to be associated in the state of vapour, the aluminium haloids, for example, can be regarded as having a very small temperature-coefficient of association, just as in the solutions investigated by the author, several salts have only a small concentration-coefficient of association. It is to be noted that these substances of small coefficient are not, in most cases, of high degree of association initially.

One effect of the study of the few metallic haloids still associated in the gaseous state has been, the author believes, to increase the difficulty of accepting the assertions variously made of the associa-

tion of all metallic salts. The tendency has been to think of association, where it has been found to exist, as concerning double molecules, rather than as being progressive.

Further, much of the previously existing evidence of the molecular condition of salts in solution has also encouraged the view that salt molecules in most cases exist as single units.

The supreme difficulty of obtaining information about the molecular size of salts lies in their lack of solubility in indifferent solvents. One method of dealing with the problem which suggested itself to the author was to make an investigation of the salts of organic bases, and then to apply the results to test such other evidence as could be obtained concerning the metallic salts. For since these bases contain alkyl groups, or, in general, organic radicles, the solution of their salts in the common indifferent solvents is more likely to be achieved than in the case of metallic haloids. Hantzsch found that dimethylamine hydrochloride was soluble in chloroform, and was able to measure its molecular complexity (*Ber.*, 1905, **38**, 1045). He found it strongly associated. Chloroform would fulfil every requirement. It belongs to the class of indifferent solvents, has a low dielectric constant (five at 20°), and, as Hantzsch showed with dimethylamine hydrochloride, gives a non-conducting solution. A test with chloroform showed that it has marked solvent power on a large number of halogen, and, indeed, on other salts of organic bases, although these same salts are, like metallic salts, either insoluble or only very slightly soluble in benzene, ether, carbon disulphide, and similar solvents. The cause of the solubility in chloroform cannot be suggested. In no case observed did combination occur with the separation of an additive product, although solutions have been kept for many months; and no separation of chloroform with the solute was observed. Tetrapropylammonium iodide, which is very soluble, was recovered from chloroform solution by evaporation at the ordinary temperature, and the product dried in the air. It gave the same results on analysis as the original substance. Supposing, however, that combination in solution occurred, the results would be lowered thereby, and tend, therefore, to mask association.

There was found available for the investigation a number of salts corresponding closely with the salts of ammonium and the alkalis. The tetraethyl- and tetrapropyl-ammonium, and the triethylsulphonium bases have been proved by Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 288) to be strong bases like the hydroxides of the alkali metals. Moreover, tetraethylammonium iodide resembles closely the corresponding salts of the alkali metals, and has been used as a normal electrolyte by Walden in numerous

investigations. The bromide and chloride have also been used, although less frequently. The data obtained, therefore, by the examination of these substances then opened up the possibility of collecting for discussion evidence concerning the molecular state of metallic salts, particularly of the alkalis, and of drawing up certain definite conclusions, not only on their molecular condition, but also on the relation of molecular association to the phenomenon of electrolytic dissociation.

The author also hoped to be able to make a comparison of the salts of bases derived from nitrogen, oxygen, sulphur, selenium, and iodine. Triethylselenium iodide was prepared, but found to undergo too easy decomposition in boiling chloroform, and its solubility in bromoform appeared to take place only at the expense of decomposition. Diphenyliodonium iodide, and the chlorides, bromides, and iodides of *o*-, *m*-, and *p*-ditolyliodonium were also prepared, but found insoluble in all reagents tested save water and alcohol.*

In addition to the substances already mentioned, the following were tested and found to be too insoluble in boiling chloroform to allow of use; ethylamine hydrochloride, tetramethylammonium chloride, bromide and iodide, aniline hydrochloride, benzylamine hydrochloride, and tetraethylammonium iodide. Aluminium and ferric chlorides are slightly soluble in chloroform, but no other metallic chloride was found to dissolve in this solvent. A number of other solvents, including bromoform, *p*-toluidine, diphenylamine, and ethylene dibromide yielded no better success.

*Notes on Materials and on the Behaviour of Certain Substances
in Chloroform Solution.*

The methyl iodide, ethyl bromide and iodide, propyl chloride, isopropyl iodide, allyl chloride, allyl iodide, bromobenzene, benzyl chloride and iodide, *p*-dibromobenzene, and *p*-iodoaniline were obtained by purchase, mainly from Kahlbaum, and were all subjected to purification. Benzyl iodide was repeatedly frozen until the melting point was constant at 23°; *p*-dibromobenzene and *p*-iodo-

* The iodonium compounds dissolve to a very slight extent in chloroform, the chlorides being most soluble, but the process of solution appears to be accompanied in all cases by decomposition. Slow evaporation yielded some solid residue with a considerable quantity of decomposition product, probably the aryl iodide. The melting points given by McCrae (*Ber.*, 1895, **28**, 97) and Heilbronner (*ibid.*, p. 1814) appear to be decomposition points pure and simple, since they could be varied over a considerable range according as heating was slow or rapid.

The author is much indebted to Miss D. M. Bennett, M.Sc., for the preparation, analysis of, and tests on the ditolyl compounds.

aniline were crystallised from alcohol. The other substances named were fractionally distilled.

Chlorobenzene and iodobenzene were prepared from aniline, and *o*-, *m*-, and *p*-iodotoluene from the corresponding toluidines.

Ortho-, meta-, and para-iodonitrobenzenes were prepared from the corresponding nitroanilines, and purified by steam distillation in slightly acid solution (a very slow process with the *m*- and *p*-compounds), and subsequent crystallisation from alcohol. Melting points: ortho-, 49—50°; meta-, 36°; para-, 172—173°.

A few of the salts were obtained by purchase, but the majority were prepared as below.

The following salts were obtained by passing dried hydrogen chloride, bromide, or iodide into a solution of the base, chloroform being the solvent used in the preparation of the first two substances below, a mixture of chloroform and benzene for dimethylpyrone, and benzene in all other cases: Triethylamine, dipropylamine, and *n*-propylamine hydrochlorides; *isobutylamine* hydrochloride and hydriodide; *isoamylamine* and *methylaniline* hydrochlorides; *ethylaniline* hydrochloride and hydriodide; *diethylaniline* hydrochloride and hydriodide; *diphenylamine*, *dibenzylamine*, *tribenzylamine*, and *phenylethylhydrazine* hydrochlorides; *quinoline* hydrochloride, *hydrobromide*, and *hydriodide*; and *dimethylpyrone* hydrochloride.

Ethylaniline hydriodide separates from benzene first as an oil. White tablets appear after a time, and crystallisation is then rapid.

With regard to *dimethylpyrone* hydrochloride, Collie and Tickle (Trans., 1889, 75, 711) found that the crystalline form with two molecular proportions of water lost hydrogen chloride on keeping, and, when desiccated for a month over sulphuric acid, lost, not only water, but an appreciable quantity of hydrogen chloride as well. The anhydrous specimen prepared as above does not suffer this loss. After keeping in a desiccator over sulphuric acid, analysis at the end of two months gave Cl=22.04, and at the end of six months 22.07, against the calculated value of 22.09 per cent.; so that no trace of decomposition was evident.

The following substances were prepared by the action of silver oxide on the iodide and neutralisation of the base: *Tetrapropylammonium* chloride, bromide, and nitrate; *triethylsulphonium* chloride and bromide. They contained no trace of iodide.

Tetraisoamylammonium iodide was prepared from *triamylamine* and *amyl iodide* at 150°, the periodide being reduced with hydrogen sulphide. It was crystallised from aqueous alcohol.

Quinoline ethiodide was also obtained from the base and *ethyl iodide*. In aqueous solution it can be titrated with silver nitrate

solution, just as in the case of the tetraethylammonium and triethylsulphonium salts.

All the salts were subjected to careful purification, either by repeated precipitation from chloroform solution by pure ether, or by crystallisation. Antimony trichloride was dried in a vacuum over sulphuric acid, then distilled, and afterwards desiccated in a vacuum over phosphoric oxide. Notwithstanding this treatment it still appeared to contain a trace of moisture, and gave a slight turbidity in chloroform. The amount was very small, and was neglected. Arsenic and antimony tri-iodides were crystallised from carbon disulphide. It may be noted, further, that acetone is a very good crystallising medium for triethylsulphonium iodide, whilst chloroform is particularly useful as a medium from which to crystallise antimony tribromide, quinoline ethiodide and hydriodide, and tetraethylammonium chloride.

Before use the salts were dried by heating at some suitable temperature, followed by desiccation in a vacuum over phosphoric oxide until constant weight was obtained. This treatment was necessary owing to the deliquescent nature of many of the substances. As a further check on their purity, the salts, with the exception of those of arsenic and antimony, were analysed immediately before the molecular-weight determinations. In drying by heat, it was found that the chlorides were always most stable, and the iodides least. The chlorides are also the most, and the iodides the least, deliquescent of the salts. Two substances, namely, triethylsulphonium bromide and iodide, were found to be more readily decomposed by heat than is generally supposed. The former suffers appreciable decomposition above 90° , whilst the latter rapidly decomposes at about 100° .

Three of the substances, diphenylamine and dimethylpyrone hydrochlorides and triethylsulphonium iodide, suffer decomposition in boiling chloroform. The two hydrochlorides emit copious fumes of hydrogen chloride, and the temperature of the solution gradually rises, so that the molecular weights recorded have no quantitative value, although they afford sure proof of strong association. It was proved, in the case of diphenylamine hydrochloride, that the decomposition is not due to traces of moisture. Triethylsulphonium iodide is more stable than the hydrochlorides named. A solution in chloroform of 2.332 grams of the substance was boiled for about twenty minutes, then carefully evaporated, and kept under diminished pressure until constant in weight. The residue weighed 1.992 grams. The actual loss during a molecular-weight determination, therefore, could not have been very great, although with such a highly associated substance the presence of small quantities of

the decomposition products, which are themselves non-associated, must reduce considerably the molecular-weight values. It would be interesting to examine the substance at a lower temperature if a suitable solvent could be found. In cold bromoform it is soluble only to a very slight extent, and is insoluble in carbon disulphide, ether, or ethylene dibromide.

The solvents used in the molecular-weight determinations were carefully purified, and the chloroform was always tested before use for traces of decomposition products. The carbon sulphide, distilled over mercury, twice over litharge, and then fractionated, and the benzene were of constant boiling point.

In calculating results, the following values of molecular elevation of boiling point or depression of freezing point were used. The boiling-point constant of carbon disulphide was tested with anthracene, and found to agree well with that of Beckmann (Beckmann, Fuchs, and Gernhardt, *Zeitsch. physikal. Chem.*, 1895, 18, 511).

Benzene (freezing point), $C=5000$.

Chloroform (boiling point), $C=3900$.

Carbon disulphide (boiling point), $C=2350$.

The Conditions Necessary for Molecular Association.

The data necessary for a solution of this question is recorded in the series of tables below. Table I embodies the results of the author's own measurements with benzene solutions of alkyl and aryl halogen compounds. As in no single instance was molecular association discovered, the results are given only in a summarised form with the values at the limits of concentration employed.

TABLE I.

Molecular Weights in Benzene of Alkyl and Aryl Halogen Compounds.

Cryoscopic Experiments.

Substance.	M. W. (calcd.).	Wt. substance per 100 grams solvent.	M. W. (obs.).
Methyl iodide	142.0	2.07—11.76	142.4—140.4
Ethyl bromide	109.0	0.96—4.87	102.5—104.2
Ethyl iodide	156.0	1.39—8.08	157.3—161.2
<i>n</i> -Propyl chloride	78.5	1.26—3.47	76.2—76.8
<i>iso</i> Propyl iodide	170.0	1.36—8.87	168.0—170.2
Allyl chloride	76.5	1.27—3.44	74.8—76.8
Allyl iodide	168.0	1.28—4.21	160.3—168.0
Chlorobenzene	112.5	1.75—7.55	110.6—114.2
Bromobenzene	157.0	1.50—6.63	154.4—157.3
Iodobenzene	204.0	2.85—12.63	200.8—205.0
Benzyl chloride	126.5	1.57—6.34	127.0—127.8

TABLE I (continued).

Substance.	M.W. (calcd.).	Wt. substance per 100 grams solvent.	M.W. (obs.).
Benzyl iodide.....	218.0	1.95—7.03	205.9—212.5
<i>o</i> -Iodotoluene.....	218.0	1.80—8.46	218.6—221.0
<i>m</i> -Iodotoluene ..	218.0	1.59—7.10	215.7—215.5
<i>p</i> -Iodotoluene.....	218.0	1.77—6.14	222.0—218.0
<i>o</i> -Iodonitrobenzene	249.0	2.29—6.88	253.4—261.9
<i>m</i> -Iodonitrobenzene	249.0	1.25—11.25	233.3—254.1
* <i>p</i> -Iodonitrobenzene	249.0	2.06	241.9
<i>p</i> -Iodoaniline.....	217.0	1.57—6.53	217.6—223.5
<i>p</i> -Dibromobenzene	236.0	2.20—7.40	213.5—233.6
Iodobenzene dichloride...	275.0	1.72	291.0

* Sparingly soluble only in cold benzene.

There is no evidence in any case of molecular association, and substitution in the benzene nucleus of groups which of themselves appear to have little or no associating power do not induce this power in the halogen atom. Iodobenzene is capable of combining with chlorine to form a dichloride, but so far as the formation of molecular aggregates is concerned, multiple valency on the part of the iodine is not exerted. Hence, in this class of compound the possession by the halogen element of latent valencies does not lead to molecular association.

In the next table, embodying the results of measurements, made by various workers, of molecular weights in solution, the review is extended to compounds of the halogens with other elements than carbon. The important point when making the selection of data was to consider the influence of the solvent in so far as it allows or hinders molecular association. A knowledge of the dielectric constant of the solvent is one guide, associating solvents having, as a rule, low values of this constant. The molecular condition of the solvent itself gives further help. Where these properties of the solvent are unknown, or where one of the rules breaks down, as in the case of nitrobenzene, which has a dielectric constant of 36.4* and yet permits association, a fairly safe guide is afforded by the practical test. Thus, Beckmann and Junker (*Zeitsch. anorg. Chem.*, 1907, 55, 371) found the dissociating power of carbonyl chloride to be very small, since it permitted very strong association of acetic and benzoic acids; and these same acids were also found to be very decidedly associated in nitrobenzene (Beckmann and Lockemann, *Zeitsch. physikal. Chem.*, 1907, 60, 385). The validity of the measurements in liquid chlorine and bromine is substantiated by the results obtained in other solvents.

* Possibly this value is too high. Beckmann and Lockemann point out that the hygroscopic nature of nitrobenzene probably accounts for the variations found in the values of the physical constants of nitrobenzene.

TABLE II.

Molecular Weights in Indifferent Solvents.

Substance.	M.W. (calc.)	Solvent.	Per cent. concn.	M.W. (obs.)
Phosphorus trichloride ¹ ...	—	Benzene	—	Normal
Phosphorus pentachloride ² —	—	Carbon tetrachloride	—	„
Arsenic trichloride ³	181·4	Benzene	—	„
—	—	Carbonyl chloride	3·39—11·1	189—194
Sulphur monochloride ⁴ ...	134·9	Bromine	0·52— 2·31	131—129
„ „ „.....	134·9	Chlorine	0·60— 1·87	127—126
Sulphur dichloride ⁵	103·0	Benzene	—	Normal
„ „ „.....	103·0	Chlorine	1·75— 3·66	108—105
„ „ „.....	103·0	Xylene	—	Normal
—	—	Ethylene dibromide	—	Normal
Iodine monochloride- α ⁶ ...	162·4	Bromoform	0·18— 0·32	166—167
Iodine monochloride- β ⁶ ...	162·4	Bromoform	0·62— 0·95	173—182
Iodine trichloride ⁷	233·4	Carbonyl chloride	0·50— 0·80	205—229
Tin tetraiodide ⁸	625·9	Benzene	3·03—19·71	613—566
Hydrochloric acid ⁹	36·46	Nitrobenzene	0·29— 2·43	148·1—51·2
„ „ „.....	—	Benzene	0·036—1·74	101·8—63·8

¹ Raoult (*Compt. rend.*, 1885, 101, 1056).² Oddo and Serra (*Gazzetta*, 1899, 29, ii, 243).³ Raoult (*loc. cit.*); Beckmann and Junker (*Zeitsch. anorg. Chem.*, 1907, 55, 371).⁴ Beckmann (*Zeitsch. anorg. Chem.*, 1906, 51, 96).⁵ Costa (*Gazzetta*, 1890, 20, 367); Beckmann (*loc. cit.*); Beckmann, Junker, and Klopfer (*Zeitsch. physikal. Chem.*, 1909, 65, 289).⁶ Walden (*Zeitsch. anorg. Chem.*, 1910, 68, 307).⁷ Beckmann and Junker (*loc. cit.*).⁸ Beckmann (*loc. cit.*).⁹ Beckmann and Lockemann (*Zeitsch. physikal. Chem.*, 1907, 60, 385).

Reference should also be made to table IX.

In addition to the compounds tabulated in this list, there are several others, namely, phosphoryl chloride and bromide, sulphuryl, thionyl, and chromyl chlorides, which might be inserted. The primary objection to their inclusion is that they contain oxygen, an element the presence of which in certain compounds gives rise to molecular association. The general rule relating to the condition required for molecular association, which is drawn up at the end of this section, applies equally well to those oxyhalogen compounds for which there is definite proof of association. Oddo and Serra (*loc. cit.*) found that all of them gave normal molecular weights in freezing benzene, but that in boiling benzene, carbon tetrachloride, and, where examined, also in carbon disulphide and chloroform, results showing distinct association were obtained. One would naturally be inclined at first to give preference to the determinations in cold benzene, but the general agreement among the values at the boiling point receives additional support in the case of sulphuryl and thionyl chlorides from measurements made on these substances in the liquid state.

The iodine monochlorides have not yet been sufficiently characterised to decide whether they are capable of association. In dilute solution the numbers do not show any marked tendency to association. Other than the oxyhalogen compounds, only one substance, hydrochloric acid, is definitely associated. It is an electrolyte.

Table III summarises our present knowledge of the molecular condition in the liquid state, as tested by well-tried methods, of a number of halogen compounds, and entirely confirms the rule, laid down at the end of this section, to which associated substances conform. Column *A* consists of the values of the degree of association calculated by Ramsay and Shields (Trans., 1893, **63**, 1099) from their own measurements, except in the case of the liquefied hydrogen haloids, the molecular state of which was ascertained by Steele, McIntosh, and Archibald (*Zeitsch. physikal. Chem.*, 1906, **55**, 145) on the basis of the Ramsay and Shields method. In column *B* are the values calculated by Walden (*Zeitsch. physikal. Chem.*, 1909, **65**, 129). The values of the degree of association of silver and of lead chlorides have been calculated from the experimental record of Lorenz and Kaufler (*Zeitsch. anorg. Chem.*, 1906, **51**, 71).

TABLE III.

Molecular Complexity in the Liquid State.

Substance.	Degree of association.		Substance.	Degree of association.	
	<i>A.</i>	<i>B.</i>		<i>A.</i>	<i>B.</i>
Methyl iodide	—	1·02	Phosphorus trichloride	1·02	0·99
Ethyl iodide	1·01—0·96	1·00	Sulphur monochloride	0·95—1·04	—
Ethyl bromide	—	1·05	Phosphoryl chloride ...	1·00	—
Ethylene dichloride ...	—	1·05	Sulphuryl chloride ...	0·97	1·02
Ethylene dibromide ...	—	1·00	Thionyl chloride	1·08	1·10
Chloroform	—	1·04	Hydrogen chloride.....	1·72	1·55
Carbon tetrachloride	1·01	0·99	Hydrogen bromide ...	1·07	1·21
Acetyl chloride	1·06	1·00	Hydrogen iodide	1·10	1·09
Chlorobenzene	1·03	—	Silver chloride	3·29	—
Silicon tetrachloride ...	1·06	1·03	Lead chloride.....	3·60	—
Tin tetrachloride	—	0·98			

Too much emphasis is not to be laid on small departures of the values of the degree of association from unity, for the results, as is known, afford only an approximate value of the molecular association. There is a consensus of evidence, however, that thionyl chloride is distinctly associated, and sulphuryl chloride is regarded by Walden also as belonging to this class. Besides these substances, there are five others, in which molecular association exists, namely, the hydrogen haloids and the salts silver chloride and lead chloride. Although there is no experimental evidence of the condition of hydrobromic and hydriodic acids in neutral solvents, there can be

little doubt from the author's measurements on salts of these acids that the acids themselves would be found, like hydrochloric, to be extensively associated. All the five associated substances, be it noted, are electrolytes.

The final table of data consists of measurements by the author of the molecular complexity of a large number of chlorides, bromides, and iodides of organic bases in chloroform solutions. The boiling-point apparatus in which the experiments were conducted has already been described (Trans., 1910, **97**, 1184). To prevent entrance of any trace of moisture it was kept closed during many of the experiments.

In the tables, the symbol *N* represents the number of milligram-molecules of the substance, calculated on the basis of the simple molecule, dissolved in 100 grams of the solvent.

In some cases the tables contain two or more series of experiments. Where this is so, the figures in italics mark the end of the series.

TABLE IV.

*Molecular Weights of Halogen Salts of Organic Bases.**Ebullioscopic Experiments in Chloroform.**n-Propylamine Hydrochloride*
(M. W. = 95.5).

<i>N</i> .	Δ° .	M. W.
16.6	0.105	588
12.7	0.079	601
15.2	0.108	524
12.8	0.094	506
10.5	0.083	474
9.2	0.077	443

isoAmylamine Hydrochloride
(M. W. = 123.6).

43.4	0.298	703
33.6	0.229	707
27.0	0.175	728
22.4	0.146	739

Diethylamine Hydrochloride
(M. W. = 109.5).

57.4	0.665	369
41.5	0.538	330
30.3	0.433	299
30.3	0.418	310
23.0	0.348	282
17.1	0.265	275

Triethylamine Hydrochloride
(M. W. = 137.6).

52.0	1.105	233
40.2	0.904	220
31.1	0.725	212
26.0	0.655	196

isoButylamine Hydrochloride
(M. W. = 109.6).

<i>N</i> .	Δ° .	M. W.
53.7	0.430	533
40.4	0.333	518
31.1	0.260	511
25.7	0.210	522

isoButylamine Hydriodide
(M. W. = 201.1).

47.6	0.259	1442
36.3	0.230	1238
28.9	0.199	1140
44.9	0.265	1328
34.3	0.227	1184
27.6	0.194	1115
23.2	0.184	990

Dipropylamine Hydrochloride
(M. W. = 137.5).

49.0	0.823	320
36.2	0.632	308
37.4	0.665	302
26.8	0.490	294
19.8	0.377	282

Triethylamine Hydrobromide
(M. W. = 182.0).

51.3	0.904	403
37.0	0.709	363
28.5	0.598	339
20.6	0.487	300
14.7	0.356	294

TABLE IV (continued).

<i>Triethylamine Hydriodide</i> (M. W. = 229.0).			<i>Tetraethylammonium Chloride</i> (M. W. = 165.6).		
N.	Δ° .	M. W.	N.	Δ° .	M. W.
34.5	0.449	686	38.8	0.257	976
27.9	0.405	616	29.5	0.210	906
22.8	0.366	555	23.6	0.183	835
19.7	0.353	498	19.4	0.157	798
23.2	0.365	571	23.5	0.172	884
17.0	0.310	491	16.0	0.145	713
12.5	0.253	440	12.1	0.121	646
<i>Tetrathylammonium Bromide</i> (M. W. = 210.1).			<i>Tetrapropylammonium Chloride</i> (M. W. = 221.7).		
37.9	0.172	1808	47.1	0.718	567
30.5	0.149	1677	33.5	0.482	601
24.7	0.138	1465	26.2	0.368	614
20.3	0.118	1410	20.3	0.271	647
<i>Tetrapropylammonium Bromide</i> (M. W. = 266.1).			21.2	0.280	654
41.2	0.443	965	17.0	0.206	716
30.2	0.318	985	<i>Tetrapropylammonium Iodide</i> (M. W. = 313.1).		
22.3	0.227	1021	42.9	0.376	1393
17.6	0.181	1011	30.4	0.267	1389
<i>Tetraisoamylammonium Iodide</i> (M. W. = 427.3).			22.5	0.201	1368
12.2	0.319	636	18.0	0.164	1337
9.28	0.270	573	13.6	0.131	1272
7.39	0.233	528	10.3	0.100	1254
<i>Ethylaniline Hydrochloride</i> (M. W. = 157.6).			<i>Methylaniline Hydrochloride</i> (M. W. = 143.5).		
28.5	0.494	354	38.3	0.610	351
21.7	0.384	346	28.8	0.479	336
18.4	0.325	348	23.5	0.398	330
15.3	0.271	346	19.1	0.345	310
<i>Diethylaniline Hydrochloride</i> (M. W. = 185.6).			16.3	0.296	308
42.5	1.046	294	<i>Ethylaniline Hydriodide</i> (M. W. = 249.1).		
31.6	0.816	280	29.1	0.498	569
22.6	0.629	261	22.8	0.413	536
17.6	0.510	256	17.6	0.327	523
<i>Diphenylamine Hydrochloride</i> (M. W. = 204.5).			15.0	0.289	504
14.1	0.291	487	<i>Diethylaniline Hydriodide</i> (M. W. = 277.0).		
11.5	0.185	496	37.0	0.649	616
<i>Phenylethylhydrazine Hydrochloride</i> (M. W. = 172.6).			27.4	0.516	575
49.4	0.621	535	20.3	0.415	528
37.6	0.522	484	<i>Dibenzylamine Hydrochloride</i> (M. W. = 233.5).		
23.5	0.333	476	3.78	0.064	481
20.3	0.318	430	2.85	0.048	478
			2.31	0.038	487

TABLE IV (*continued*).

<i>Quinoline Hydrochloride</i> (M. W. = 165.5).			<i>Tribenzylamine Hydrochloride</i> (M. W. = 323.6).		
N.	Δ° .	M. W.	N.	Δ° .	M. W.
74.7	1.102	438	14.5	0.460	397
55.5	0.869	413	12.3	0.387	401
41.8	0.699	386	10.5	0.338	393
44.5	0.741	388	9.2	0.296	392
32.4	0.560	373	<i>Quinoline Hydrobromide</i> (M. W. = 210.0).		
26.1	0.501	336	52.0	0.641	664
21.9	0.431	328	37.8	0.522	593
<i>Quinoline Hydriodide</i> (M. W. = 258.0).			29.9	0.436	561
5.24	0.127	414	38.1	0.525	595
4.24	0.115	369	26.9	0.415	530
3.60	0.115	315	20.3	0.347	480
3.01	0.102	297	<i>Quinoline Ethiodide</i> (M. W. = 285.0).		
<i>Triethylsulphonium Chloride</i> (M. W. = 154.6).			4.69	0.076	687
36.7	0.310	714	3.41	0.069	550
27.8	0.264	636	2.84	0.066	479
21.7	0.212	617	2.39	0.056	474
17.6	0.177	599	2.09	0.051	456
<i>Triethylsulphonium Iodide</i> (M. W. = 246.1).			<i>Triethylsulphonium Bromide</i> (M. W. = 199.1).		
50.7	0.165	2951	42.7	0.244	1359
37.6	0.160	2258	31.7	0.212	1161
40.3	0.142	2735	24.9	0.199	972
30.9	0.142	2089	31.3	0.207	1172
23.5	0.128	1765	25.0	0.192	1010
			20.2	0.165	949
			<i>Dimethylpyrone Hydrochloride</i> (M. W. = 160.5).		
			30.1	0.609	310

It is not proposed in this section to enter into a close analysis of the results just given. It is sufficient for the present purpose to emphasise what is readily obvious, that molecular association of a very pronounced type is shown by these halogen salts. In the majority of instances, the most concentrated solution does not reach 10 per cent., and in a number of cases it is less than 5 per cent., yet the association in the dilute solutions is much greater than that which substances such as organic acids, alcohols, phenols, amides, etc., show in concentrated solution.

At the foot of tables II and III it has been pointed out that the substances which give evidence of molecular association are either electrolytes or conducting media. Combine now the whole of the results detailed in this paper, and this statement will be found a rule without exception. Even the oxychlorides already alluded to in table II afford no exception to the rule, and at once are associated substances and capable of transmitting a current of electricity.

The fact that associated liquids form good conducting media is well known. It was pointed out by Crompton in 1897 (*Trans.*, 1897, **71**, 945), and re-stated in modified form by Dutoit (with Aston, *Compt. rend.*, 1897, **125**, 240; with Friderich, *Bull. Soc. chim.*, 1898, [iii], **19**, 321). As will be evident by the results now brought forward, conducting solutes, or electrolytes, must also be capable of association; at any rate, when in the free state. And it may be pointed out in this connexion that even acetamide, ethyl alcohol, and other organic compounds capable of association, although they are not electrolytes in the ordinary sense of the term, considerably augment the conductivity of the liquid halogen haloids when dissolved in the latter (Steele, McIntosh, and Archibald, *loc. cit.*; Beckmann and Waentig, *Zeitsch. anorg. Chem.*, 1910, **67**, 17).

The conductivity and the degree of association of organic liquids do not always run in the same order (Walden, *Zeitsch. physikal. Chem.*, 1903, **46**, 103). The connexion between the two is best displayed in series of similar substances. Again, the conductivity of organic substances, however highly associated, bears no comparison with that of fused salts. The halogen-containing compounds do afford an excellent example, perhaps better than any other at present known, of the frequently found relationship between conductivity and molecular association. Table V, which follows, supplies the illustration, and helps to prove, what it is the purpose of this section to show, that molecular association among halogen-containing compounds only occurs when the substance is a conductor of electricity.

Two of the substances mentioned in the table, namely, arsenic trichloride and antimony trichloride, have not previously been mentioned, but data concerning their molecular state are quoted in tables VII and VIII. As to the conductivities, most of the values were measured by Walden (*Zeitsch. anorg. Chem.*, 1902, **29**, 371). In addition, the ionising power of the solvents, measured by their effect on tetraethylammonium iodide, was also tested by him, and found in perfect agreement with the measurements on the medium alone.

In the table, x is the degree of association in the liquid state, λ the conductivity in reciprocal ohms.

TABLE V.

Comparison of Conductivity and Degree of Association.

A. Non-associated substances.

Substance.	λ .
PCl ₃	0
S ₂ Cl ₂	0
SiCl ₄	0
SbCl ₅	0
SnCl ₄	0
AsCl ₃	1.24×10^{-6}

B. Associated substances.

Substance.	α .	λ .
SO ₂ Cl ₂	1.02	0.18×10^{-6}
SOCl ₂	1.10	2.0×10^{-6}
POCl ₃	— ¹	2.2×10^{-6} ²
SbCl ₃	— ³	109×10^{-6} (80°)
AgCl	2.25 ⁴	1.83 ⁵ (500°)
PbCl ₂	2.3 ⁴	2.39 ⁵ (520°)
KCl	8 ⁴	1.91 ⁵ (750°)
NaCl	10 ⁴	3.84 ⁵ (750°)

¹ Oddo and Serra (*loc. cit.*); Walden (*Zeitsch. Elektrochem.*, 1909, **14**, 715).² See also Oddo (*Atti R. Accad. Lincei*, 1901, [v], **10**, i, 452); Walden (*Zeitsch. anorg. Chem.*, 1910, **68**, 307).³ See Table VII.⁴ Table IX.⁵ Landolt-Börnstein, *Tabellen*, 1905.

The above table, it will be seen, is entirely of inorganic liquids. The non-associated halogen compounds of carbon are generally recognised as non-conductors.

In the table, the only non-associated substance showing conductivity is arsenic trichloride. Although small, the conductivity is quite definite. It may be remarked, however, that the detection of conductivity is infinitely easier than the decision, whether a substance is or is not associated.* All associated substances are however, conductors, and the best conductors are the substances which are most associated.

Other examples can be quoted of this connexion between conductivity and association. One will suffice. The liquid hydrogen haloids are comparatively but poor conductors (Steele, McIntosh, and Archibald, *loc. cit.*; Beckmann and Waentig (*loc. cit.*). In accordance with this, their degree of association is also small. The parallelism between the two properties can be traced still further with hydrogen chloride; for, when dissolved in nitrobenzene, both conductivity and degree of association decrease as the concentration is increased (Beckmann and Lockemann, *loc. cit.*). Thus, there is here perfect agreement between conductivity and molecular association.

All the preceding evidence points, therefore, to the fact that a halogen-containing substance, to be capable of molecular association, must be electrically active: either a conducting medium or an electrolyte. Further, the expectation of finding molecular association among the halogen-containing substances, based on the view

* Although arsenic trichloride is called a non-associated substance, the molecular weight values found by Beckmann and Junker are somewhat above the normal.

that the halogen elements have latent valencies capable of chemical activity, have not been realised, except on the condition named. The electrical behaviour of a substance is the only single criterion by which the possibility of molecular association can be safely predicted.

Of equal importance to the establishment of the conditions necessary for association is the fact which now comes to light that molecular association appears as the inverse of electrolytic dissociation or ionisation. Salts which, in solvents of low dielectric constant (for example, chloroform) are associated, display the phenomenon of electrolytic dissociation when dissolved in liquids of high dielectric constant. Using the terms in their commonly accepted sense, we may say, with the knowledge that the converse is also true, no ionisation, no association.

The Molecular Size of Haloid Salts of Organic Bases.

In order to ascertain, so far as the data allow, the factors that govern the extent of the molecular association of these salts, a closer examination will here be made of the experimental values already recorded. Immediately following is a table summarising these results, the concentrations being expressed in terms of grams of solute per 100 grams of solvent. Under *A* are given the association factors calculated for the extremes of concentration. The salts have also been more accurately compared at a common molecular concentration of 25 milligram molecules per 100 grams of solvent. The symbol A_{25} represents the degree of association at this concentration. For a substance of formula weight 200, this strength of solution corresponds approximately with 5 per cent., and is therefore covered by the term "dilute."

In order to afford comparison with diethyl and dipropylamine hydrochlorides, there has been added to the table, after recalculation to the author's standards, the results of Hantzsch's measurements on dimethylamine hydrochloride.

The two substances, diphenylamine hydrochloride and dimethylpyrone hydrochloride, which undergo decomposition in boiling chloroform are not included.

The numbers enclosed in brackets must be considered as approximate only. Propylamine hydrochloride is so slightly soluble, and the elevation of boiling point is consequently so small, that a small experimental error in the measurement of temperature will have a large effect on the molecular weight calculated. In the case of tetra-amylammonium iodide, lack of material prevented determinations at higher molecular concentrations.

TABLE VI.

Molecular Size in Chloroform of Halogen Salts of Organic Bases.

Substance.	M.W. (calc.)	Concentration.	M.W. (obs.)	A.	A ₂₅ .
<i>n</i> -C ₃ H ₇ ·NH ₂ , HCl ...	95·5	0·88—1·58	443—588	4·6—6·2	(8)
<i>iso</i> -C ₄ H ₉ ·NH ₂ , HCl ...	109·6	2·81—5·88	522—533	4·77—4·87	4·63
<i>iso</i> -C ₄ H ₉ ·NH ₂ , HI	201·1	4·67—9·58	990—1443	4·93—7·17	5·37
<i>iso</i> -C ₅ H ₁₁ ·NH ₂ , HCl ...	123·6	2·77—5·37	739—703	5·98—5·67	5·92
NHMe ₂ , HCl	81·5	0·47—3·18	227—333	2·78—4·09	3·92
NHEt ₂ , HCl	109·5	1·87—6·29	275—369	2·51—3·37	2·63
NHPr ₂ , HCl	137·5	2·72—6·75	282—320	2·05—2·35	2·11
NEt ₃ , HCl	137·6	3·58—7·11	213—253	1·55—1·84	1·62
NEt ₃ , HBr	182·0	3·74—9·34	294—403	1·64—2·22	1·78
NEt ₃ , HI	229·0	4·51—7·90	498—686	2·17—3·00	2·52
NEt ₄ Cl	165·6	2·00—6·43	646—976	3·90—5·90	5·12
NEt ₄ Br	210·1	4·26—7·97	1410—1794	6·71—8·60	7·2
NPr ₃ Cl	221·7	3·78—10·43	716—517	3·23—2·56	2·78
NPr ₄ Br	266·1	4·70—10·95	1011—965	3·80—3·63	3·76
NPr ₄ I	313·1	3·21—13·42	1254—1393	4·00—4·45	4·40
N(C ₅ H ₁₁) ₄ I	427·3	3·15—5·17	528—636	1·24—1·49	(2·17)
NHPhMe, HCl	143·5	2·33—5·50	308—351	2·15—2·45	2·31
NHPhEt, HCl	157·6	2·40—4·49	346—353	2·20—2·25	2·22
NHPhEt, HI	249·1	3·73—7·51	504—569	2·19—2·46	2·19
NPhEt ₂ , HCl	185·6	3·35—7·88	256—294	1·38—1·58	1·43
NPhEt ₂ , HI	277·0	5·62—10·25	528—616	1·91—2·22	2·04
NH(CH ₂ Ph) ₂ , HCl ...	233·5	0·48—0·79	487—481	2·06	(?)
N(CH ₂ Ph) ₃ , HCl	323·6	2·98—4·68	392—397	1·21—1·23	1·26
NHPh·NEt, HCl ...	172·6	3·50—8·52	430—535	2·49—3·10	2·57
C ₉ H ₇ N, HCl	165·5	3·62—12·37	328—437	1·98—2·64	2·07
C ₉ H ₇ N, HBr	210·0	4·27—10·92	480—664	2·29—3·16	2·48
C ₉ H ₇ N, HI	257·0	0·78—1·35	297—414	1·44—1·61	(?)
C ₉ H ₇ NEtI	285·0	0·60—1·34	456—687	1·6—2·4	(?)
SEt ₃ Cl	154·6	2·72—5·68	599—714	3·87—4·62	4·0
SEt ₃ Br	199·1	4·02—8·50	949—1359	4·77—6·83	5·0
SEt ₃ I ..	246·1	5·73—12·48	1765—2951	6·7—12·0	7·6

Comparing the different salts with one another it will be seen that in nearly all cases the degree of association increases with the concentration. Exceptions to the rule are *iso*amylamine hydrochloride and tetrapropylammonium chloride. The behaviour of these substances, although somewhat unusual, resembles that of hydrochloric acid in benzene and in nitrobenzene solutions (Beckmann and Lockemann, *loc. cit.*).

The coefficient of increase of association with concentration is also subject to variation from substance to substance. Tetrapropylammonium iodide has a comparatively small coefficient, and two or three of the hydrochlorides (notably ethylaniline hydrochloride) have coefficients of still smaller value. Allowing for experimental error, it is found in many cases that the curve connecting the molecular weight with the concentration is a straight line; or, the association is a linear function of the concentration.

As to the factors determining the extent of association, an inspection of the degree of association of the different salts shows that

the association is dependent on two factors, the one for the acid, the other for the base. Turning first to the question of the effect of the acid it will be seen throughout that the chlorides are least associated, the iodides most. The list of association factors at the comparison concentration contains one case which does not appear to bear out this rule, for the degree of association of ethylaniline hydrochloride is slightly greater than that of the hydriodide. A closer inspection will reveal the fact that the association of the hydrochloride alters but slightly with the concentration, whilst that of the hydriodide is subject to much greater variation, so that at a higher concentration than the one chosen for comparison the order is reversed.

The ratios between the values of A for the chloride, bromide, and iodide vary from salt to salt, and no general rule is observable. It has to be remembered, however, that the comparison concentration is chosen quite arbitrarily.

The predominating factor in the association of salts appears to be the base. As regards the basic tendencies of nitrogen, oxygen, sulphur, etc., experimental difficulties have prevented a comparison, except of nitrogen and sulphur bases. Here we find, from the comparison of the tetraethylammonium and the triethylsulphonium salts, that the nitrogen bases produce the more strongly associated salts.

Of nitrogen bases alone there is a long list available for comparison, and when these are studied it is found that the mass of the base has a very marked effect on the association of the salt. The salts derived from the monoalkylamines are most strongly associated, then follow the salts from the dialkyl-, and last, in degree of association, those derived from the trialkyl-amines. Further illustration may be had by a study of dimethyl-, diethyl-, and dipropyl-amine hydrochlorides; di- and tri-benzylamine hydrochlorides; and tetraethyl- and tetrapropyl-ammonium chlorides. Again, tetra-isoamylammonium iodide, the base of which has a high molecular weight, is not very strongly associated as compared with other iodides.

The effect of the base on the association of the salt is not proportionate to its mass, as will be observed by comparing the salts of the aliphatic and aromatic amines. It depends both on the size and the number of the groups which have substituted hydrogen in the amine. In passing, however, from the tri-substituted amine to tetra-substituted ammonium, the association of the salt shows a decided increase instead of a decrease. Quinoline ethiodide in the same way is more associated than quinoline hydriodide.

We might reasonably expect to find, therefore, that the effect

of the base on the association of its salts would run parallel with its strength. So far as the tetra-substituted ammonium and the trialkylsulphonium bases are concerned, this expectation is realised, these bases being strong, like the alkaline hydroxides. As regards the other salts, however, there appears to be no connexion between the degree of association of the salt and the strength of the base as measured by the dissociation constant in aqueous solution (Bredig, *loc. cit.*). The monoalkylamines, for example, are considerably weaker than the dialkyl, but their effect on the association of salts derived from them is in the reverse order.

There does appear, however, to be an approximate agreement between the degree of association of the salt and the dielectric constant of the base, assuming the latter to be of the NX_3 type. The ammonium salts also would probably be capable of classification in this way. Whether the agreement is more than accidental it is not possible to decide, the data concerning the dielectric constants being too incomplete.

The rules which it may be said with certainty are obeyed by the halogen salts of organic bases are:

- (1) Molecular association always occurs.
- (2) The degree of association depends on two factors, one for the acid, the other for the base.
- (3) The extent of association increases in the order



that is, with increase in the mass of the halogen; and,

- (4) Decreases, when salts from similarly constituted bases are concerned, with the mass of the base.

The Molecular Condition of Metallic Halogen Salts.

Since some of the most important questions in theoretical chemistry are centred in the problem of the molecular complexity of metallic salts, many attempts have been made to settle their actual molecular condition. All the systematic investigations on this subject have dealt with the problem as presented by the chlorides, bromides, and iodides, and the present inquiry is also limited to this class of salt.

This present section resolves itself into three parts: (a) a critical examination of previous investigations, which appear at first sight to disfavour the conclusion that metallic salts are associated; (b) a review of indirect evidence, which most strongly points to association occurring; (c) an endeavour both to discover the rules concerning the association of these salts and to establish the relationship between molecular association and electrolytic dissociation.

Much of the evidence on the molecular condition of metallic salts appears undoubtedly to ascribe to them the simple unimolecular formulæ by which, as a rule, they are represented. The determinations of the molecular weight of metallic chlorides, however, in boiling piperidine, pyridine, methyl and ethyl sulphides, etc., by Werner and his pupils (*Zeitsch. anorg. Chem.*, 1897, **15**, 1); in boiling quinoline (Beckmann, *ibid.*, 1907, **55**, 236), and in freezing mercuric chloride (Beckmann, *ibid.*, 1907, **55**, 175); in boiling bismuth chloride by Rügheimer (*Ber.*, 1903, **36**, 3030) and Rügheimer and Rudolfi* (*Annalen*, 1905, **339**, 311); in fused salt hydrates by Morgan and Benson (*Zeitsch. anorg. Chem.*, 1907, **55**, 261); in urethane by Castoro (*Gazzetta*, 1898, **28**, [ii], 317), one and all have not only led to the present adoption of the unimolecular formulæ for the salts investigated: they have, in the author's opinion, gone further than this in masking the association of salts which other evidence declares to exist. The results of the above investigations do not make it necessary, however, to assume the physical indifference to one another of salt molecules, and the following suggestions, whilst they do not pretend to solve all the difficulties involved, do indicate, nevertheless, that the bulk of the evidence cited above should not be taken as evidence that salts are non-associated substances.

The results of a molecular-weight determination must depend on two factors: on the medium and on the temperature. The third factor, the concentration, need not be considered here. As regards the medium, the Neinst-Thomson rule (J. J. Thomson, *Phil. Mag.*, 1893, [v], **36**, 313; Nernst, *Zeitsch. physikal. Chem.*, 1894, **13**, 535) asserts that dissociation of the solute will be allowed or restricted according as the dielectric constant of the solvent is high or low, and, conversely, association is allowed to the fullest extent by a medium of low dielectric constant. This rule can be shown to represent the general experience. So far as association is concerned, it was tested by Meldrum and Turner (*Trans.*, 1908, **93**, 876; 1910, **97**, 1605) in connexion with the amides, and found to hold for five solvents used. Other examples of the operation of this rule can be furnished where the solutes concerned are salts. Thus, according to the author's measurements, tetraethylammonium iodide should be very highly associated in chloroform, the dielectric constant of which is 5 (at 22°); in pyridine, of dielectric constant 20 (at 20°), this salt is very much less associated (Walden and Centnerszwer, *Zeitsch. physikal. Chem.*, 1906, **55**, 321). Again, in ethyl alcohol, of dielectric constant 26, lithium chloride appears to

* Although all the chlorides used had normal molecular weight in bismuth chloride solution, Rügheimer, on other considerations, expresses the view that many metallic chlorides are really associated.

be dissociated (Beckmann, *Zeitsch. physikal. Chem.*, 1890, **6**, 460), but in amyl alcohol, of dielectric constant 15.9, Andrews and Ende (*Zeitsch. physikal. Chem.*, 1895, **17**, 144) found pronounced association. A comparison of certain of the author's values in chloroform with those in liquid sulphur dioxide obtained by Walden and Centnerszwer (*Zeitsch. physikal. Chem.*, 1901, **39**, 578) bears out the rule. Finally, the principle is established by the very fact that the salts of organic bases investigated by the author are readily ionised by water, and strongly associated in chloroform. We might, in fact, use the principle thus established to prove that the substances which are electrolytically dissociated in solvents of high dielectric constant must be associated in those of low dielectric constant, although the original rule probably did not intend this interpretation.

Another factor besides that of dielectric constant must be considered. The solvent should also be indifferent towards the solute in the sense that chemical action should not occur. Wherever chemical combination in solution takes place, the molecular-weight results are lowered.

If we examine in the light of these arguments the investigations cited above, we find that piperidine and pyridine both have somewhat high dielectric constants. No electrolytic dissociation was found by Werner, but the dissociating power of pyridine on molecular complexes has already been shown in connexion with tetraethylammonium iodide. Moreover, resorcinol and organic acids, which are strongly associated in naphthalene and in benzene, have the normal molecular-weight values in pyridine (Innes, *Trans.*, 1901, **79**, 265). Further, Werner found that the solvents he used formed, in many cases, definite compounds with the solutes, which must lead, as Kohler proved (*Amer. Chem. J.*, 1900, **24**, 385), to low values of the molecular weight. Thus, aluminium bromide in carbon disulphide had the formula Al_2Br_6 ; but in nitrobenzene, with which it forms a definite compound, its molecule corresponds with AlBr_3 . In spite of chemical combination, it may be noted that, like tetraethylammonium iodide in pyridine, the haloids of silver, which belongs to the first group in the periodic table, show pronounced association in piperidine (Werner, *loc. cit.*).

Some of the arguments raised against the use of pyridine probably also apply to quinoline (Beckmann, *loc. cit.*). As regards the use of mercuric chloride and bismuth chloride as solvents, we have no knowledge of their dielectric constants. From evidence given below, however, it is certain that both are to some extent associated substances, and, according to general experience, associated substances do not appear to be associated in associated solvents.

Again, like the chlorides of mercury and bismuth, urethane, used by Castoro as a solvent, is decidedly associated; and salt hydrates exert a dissociating influence, glycerol and glycol, for example, having normal molecular weights in the solvents used by Morgan and Benson.

Finally, in connexion with the fact that Nernst (*Zeitsch. Elektrochem.*, 1903, **9**, 622) found the vapours of sodium chloride and potassium chloride at temperatures approaching 2000° to consist mainly of simple molecules, it may be urged that such evidence does not deny the possibility of association at lower temperatures. Whether a substance, associated when liquid, will still be found associated in the state of vapour depends on the temperature-coefficient of association, and less on the initial degree of association. The molecular aggregates of liquid formamide, which is highly associated, break up rapidly with increasing temperature. Water is strongly associated as a liquid, but not when vaporised. On the other hand, acetic acid, the degree of association of which is much less susceptible to change of temperature, is still associated in the state of vapour, provided the temperature is not too high.

Certain indirect evidence which strongly points to the association of metallic salts is now brought forward.

1. *Evidence from Solubility.*—The fact that most metallic salts do not dissolve in indifferent solvents, whilst preventing accumulation of direct evidence, does, in itself, afford certain indirect evidence of the molecular state of these substances. Crompton pointed out (*Trans.*, 1897, **71**, 939) that unimolecular liquids mixed readily, but the solubility of unimolecular and associated substances one in the other appeared to be limited. Although molecular complexity may not be the only factor determining solubility—the influence of mass, for example, quite apart from its effect on association, cannot be neglected—it appears to be one of the main factors, and the rule is a fairly trustworthy guide where other evidence is wanting. It has been abundantly verified during the course of investigations in which the author has been engaged. In the light of the association factors of salts quoted in this paper, additional support can be obtained from Walden's investigations on solubility (*Zeitsch. physikal. Chem.*, 1906, **55**, 683; 1908, **61**, 633).

Associated substances, it will be found, do not readily dissolve in the solvents which make that association manifest. This rule holds, both for ordinary association and for association in water (Meldrum and Turner, *Trans.*, 1910, **97**, 1805; Peddle and Turner, this vol., p. 685). So far as organic substances are concerned, it will suffice, although there are many examples, to quote the

immiscibility of formamide, acetamide, sulphuric acid, water, glycol, glycerol, and the sugars, with liquids such as benzene, chloroform, carbon disulphide, etc. With respect to association in water, examples have been pointed out recently (Peddle and Turner, *loc. cit.*). Passing on to the salts of organic bases which have been examined in connexion with the present investigation, the same rules hold. All are soluble in water; generally speaking, the more associated the substance the more soluble in water. On the other hand, the salts are insoluble, or but very sparingly soluble, in benzene, carbon disulphide, ether, etc. Tetra-amylammonium iodide, which is not strongly associated, is much less soluble in water, but much more soluble in benzene, than the strongly associated salts. Even solubility in chloroform does not, in one sense, depart from the rule, for here it is found, especially if similar substances are compared, that the more associated the salt the smaller its solubility. Thus, solubility increases in the order ethylamine-, propylamine-, butylamine hydrochloride; dibenzylamine-, tribenzylamine hydrochloride; again, tetraethylammonium iodide is not soluble to the extent of 0.5 per cent. in boiling chloroform, whereas tetrapropylammonium iodide is readily soluble; and finally, among other examples, iodides are much less soluble than chlorides. In all these cases, the least soluble substance is the most strongly associated.

If we apply these rules now to the metallic haloids, the ready solubility of these substances in water and their insolubility in the indifferent solvents, renders it highly probable that the haloid salts are associated. Leaving out of consideration those solvents which it has been proved owe their solvent power to combination with the solute, metallic salts dissolve most readily in water and in formamide (compare Turner and Merry, *Trans.*, 1910, **97**, 2069). From tables VII, VIII, and IX an idea of the relative degree of association of the different salts can be obtained, and it will be found, on the whole, that the most associated salts are most easily soluble in water (alkali haloids), and are insoluble in indifferent solvents. Less associated substances are more soluble in ethyl alcohol than the alkali chlorides; such substances, for example, as the haloids of iron, aluminium, mercury (Hg^{++}). Aluminium bromide and iodide are even soluble in carbon disulphide, and so, also, to some extent are the mercuric haloids. Prideaux concluded from measurements of Trouton's constant (*Trans.*, 1910, **97**, 2039) that of the mercuric haloids the chloride is most, and the iodide least associated. This conclusion accords with solubility data as interpreted here, for mercuric chloride is most soluble in water and the iodide least, the order being reversed when carbon disulphide is the solvent.

Finally, the non-associated or only slightly associated haloids of the metalloids arsenic and antimony are hydrolysed by water, but are soluble in a number of indifferent solvents, such as benzene and carbon disulphide.

Solubility data may, therefore, be interpreted in such a way as to give some indication of the degree of association of a salt.

2. *Evidence from Molecular-weight Determinations in Water.*—Molecular-weight determinations of organic substances in water yield, where the substance is readily soluble, normal results, supposing only dilute solutions to be considered. More recently it has been shown (Meldrum and Turner, *loc. cit.*; Peddle and Turner, *loc. cit.*) that the more nearly normal a substance is when in the free state or when dissolved in indifferent solvents, the more does it appear to be associated in water. We can apply this fact to mercuric chloride, which is a non-electrolyte. Practically all salts give abnormally small molecular weights in water, but Beckmann (*Zeitsch. physikal. Chem.*, 1890, **6**, 460) and Kahlenberg (*J. Physical Chem.*, 1901, **5**, 367) have found that mercuric chloride is distinctly associated in water, a result which proves that in the free state, as also in indifferent solvents, this substance must be considerably less associated than most metallic salts. This conclusion is in agreement with that of Prideaux formed on other evidence.

3. *Evidence from the Results with the Salts of Organic Bases.*—The resemblance between the salts of the alkalis and those of the nitrogen bases discussed in the earlier sections of this paper, need not be emphasised. Whether we regard the ammonium salts as being at the head of the series of amine salts, or most like the tetra-substituted ammonium salts, the evidence admits of no other conclusion than that ammonium chloride, bromide, and iodide must be strongly associated. And if the ammonium salts are associated, then we may expect the corresponding salts of the alkalis to be likewise associated.

Again, it is possible to prepare periodides of the types MI_3 , MI_5 , MI_7 , MI_9 in nitrobenzene solution (Dawson and Goodson, *Trans.*, 1904, **85**, 796; Dawson and Jackson, *ibid.*, 1908, **93**, 2063), where M represents the alkali metals, ammonium, tetraethyl- and tetrapropyl-ammonium. Evidence will be brought forward in another communication to show that this kind of association, namely, association with iodine, is a measure of the power of the individual salt molecules to unite with one another. As also the property of forming periodides is greatest with the most strongly electropositive metals (Abegg and Hamburger, *Zeitsch. anorg. Chem.*, 1906, **50**, 403; Olivari, *Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 584, 717),

it is not unreasonable to conclude that the haloid salts of the alkalis are more strongly associated than those of any other metals. Mercuric iodide, according to Olivari, forms no periodide.

Such direct evidence will now be cited as will suffice to prove that metallic haloids are associated, and allow one to test whether the rules drawn up for the salts of organic bases hold also for metallic salts.

Table VII contains the results of the limited measurements which the author found it possible to make in indifferent solvents. The determinations were carried out at the boiling point of the solvent.

TABLE VII.

Molecular Weights in Carbon Disulphide.

<i>Arsenic Tri-iodide</i> (M. W. = 455.7).			<i>Antimony Tri-iodide</i> (M. W. = 501).		
N.	Δ° .	M. W.	N.	Δ° .	M. W.
21.7	0.499	466	7.06	0.168	495
19.1	0.442	462	6.17	0.148	497
17.5	0.413	452	5.50	0.129	502
15.7	0.369	455	4.90	0.125	462
13.8	0.334	443			
12.4	0.300	442			

Molecular Weights in Chloroform.

<i>Antimony Trichloride</i> (M. W. = 226.6).			<i>Antimony Tribromide</i> (M. W. = 360).		
N.	Δ° .	M. W.	N.	Δ° .	M. W.
49.0	1.527	284	27.5	0.921	420
39.9	1.297	272	23.0	0.790	408
33.0	1.084	269	19.2	0.669	402
28.2	0.951	262	16.3	0.581	393
			14.2	0.520	383

Arsenic tri-iodide is not associated. Antimony trichloride and tribromide are both somewhat associated. At a concentration of 25 milligram-molecules per 100 grams of solvent, the association factor of the chloride is 1.14, that of the bromide 1.15, so that there is little difference between them. The tri-iodide does not appear to be associated, although concentrated solutions could not be obtained.

Tables VIII and IX summarise data drawn from various sources, and allow a number of conclusions to be drawn. In table VIII the solvents selected are those which do not possess very high dielectric constants. The actual values of this constant are given side by side with the solvent. Objections might be raised against the solvent sulphur dioxide on the score that Walden and Centnerszwer (*Zeitsch.*

physikal. Chem., 1903, **42**, 432) had reason to suspect, in certain cases, that sulphur dioxide was capable of combining with the solute. When all has been said, however, this circumstance strengthens the proof of association, since, if association be evident at all, it must be considered only as a reduced value of the true association.

TABLE VIII.

Molecular Weights in Solution of Metallic Haloids.

A.—Non-associated Substances.

Substance.	Solvent.	Dielect. constant.	Observer.
AsCl ₃	Benzene	2.3	Raoult (see table II.)
—	Carbonyl chloride	?	Beckmann and Junker
AsI ₃	Carbon disulphide	2.6	} Turner
SbI ₃	"		
SbCl ₅	Carbonyl chloride		
SnI ₄	Benzene	2.3	Beckmann and Junker
			Beckmann

B.—Associated Substances.

Sub- stance.	Solvent.	D.C.	Concn.	A.	Observer.
SbCl ₃	Chloroform	5.0	6.4 — 11.1	1.16—1.25	Turner
—	Carbonyl chloride	?	0.60—3.04	1.07—1.12	Beckmann & Junker
—	Ether	4.4	?	1.01—1.19	Lespieau
SbBr ₃	Chloroform	5.0	5.1 — 9.9	1.06—1.19	Turner
HgCl ₂	} Ether	4.4	?	1.13—1.31	Lespieau ¹
ZnCl ₂			?	1.66—3.91	" ²
FeCl ₃			?	1.0 — 1.11	" ²
AlBr ₃	} Carbon disulphide	2.6	1.5 — 10.9	2.0 (approx.)	} Kohler
AlI ₃ ...			2.5 — 10.7	2.0 (approx.)	
LiCl...	Amyl alcohol	15.9	0.66—6.0	0.94—1.7	Andrews & Ende
NH ₄ I	} Sulphur dioxide	13.75	Normal solutions	2.44	} Walden and Centnerszwer
KI ...				2.38	
RbI ...				1.92	

¹ *Compt. rend.*, 1897, **125**, 1094.

² See also Muller, *Compt. rend.*, 1894, **118**, 644.

From table VIII it is evident that the salts of the alkali metals must be strongly associated, especially when we take into account the considerable dielectric constants of amyl alcohol and sulphur dioxide. Probably, also, the degree of association of mercuric chloride is somewhat greater than indicated by the measurements in ether.

Table IX summarises a number of values of the molecular complexity in the liquid state. Column I contains numbers given by Lorenz and Kaufler (*loc. cit.*) calculated by the Ramsay and Shields' formula. The values in column II were calculated by Walden (*Zeitsch. Elektrochem.*, 1908, **14**, 715) from the experiments of

various workers, on the basis of the formula $\frac{Ma_{\phi}^2}{T_{\phi}} = \text{constant}$, repre-

senting the relationship between the molecular cohesion and the melting point on the absolute scale. Walden found that the equation gave results for a large number of organic and non-metallic compounds in fair agreement with those calculated by other means, and that it was free from the objections which have been raised against the Ramsay and Shields' formula (compare Walden, *Zeitsch. physikal. Chem.*, 1909, **65**, 129; *ibid.*, 1910, **75**, 555; Turner and Merry, *Trans.*, 1910, **97**, 2069). The results in the case of salts received confirmation from measurements of the latent heat of fusion.

TABLE IX.

Molecular Complexity of Fused Salts.

Substance.	Degree of association.		Substance.	Degree of association.	
	I.	II.		I.	II.
NaCl	—	{ 10.0 8.0	KI	—	{ 6.0 4.0
NaBr	—	8.0	CdCl ₂	—	5.0
NaI	—	6.2	PbCl ₂	3.60	2.3
KCl	—	{ 8.0 6.0	PbBr ₂	—	2.2
KBr	—	7.0	AgCl	3.29	2.25
			SbBr ₃	—	1.3

Tin tetrachloride, quoted in table III, may also be taken into account here.

Without further detailed criticism of these tables, all the evidence contained in this section leads, the author believes, to the following conclusions.

1. Metallic haloid salts are associated substances.

The evidence appears to indicate that as we pass from left to right in the periodic table, the power of association of the haloids diminishes. On the one hand, we have the alkali chlorides as the most strongly associated substances; on the other, the chlorides of carbon, silicon, phosphorus, sulphur, and iodine are non-associated. Zinc and cadmium chlorides are less associated than those of the alkalis, but more than the aluminium halides.

As the metallic character of the element grows, the tendency of the salt to associate also increases. (Compare the haloids of phosphorus, arsenic, and antimony.)

2. The degree of association depends on both the acid and the base. It rises in the order

Iodide → Bromide → Chloride.

In this respect the metallic halides do not appear to behave like the salts of organic bases. All available evidence, however, points to the metallic chlorides being most associated, and the iodides least. (Compare salts of sodium, potassium, lead, mercury (Hg⁺⁺), and antimony.)

3. In a series of similar salts the degree of association decreases with increase in the atomic weight of the metal. (Compare the salts of the alkalis, zinc, and mercury.)

Here there is close agreement with the salts of organic bases.

All these conclusions are in agreement with previously disclosed evidence that molecular association is complementary to electrolytic dissociation. Thus, Abegg and Bodländer (*Zeitsch. anorg. Chem.*, 1899, **20**, 453) drew the conclusion that the power of ionisation possessed by the metals in salts of a common acid decreases as we pass from left to right in the periodic table. The evidence in the case of molecular association is much less complete, but what there is presents a close parallel with the tendency to become ionised. Further, if we accept conclusion (2) as correct, it also falls into line in that Abegg and Bodländer state that chlorides have the strongest and iodides the least tendency to become ionised. Again, in the series of the alkali salts, ionisation diminishes with increase in the atomic weight of the metal; the same order, therefore, as for molecular association.

One further test of this parallelism is revealed by a study of the results of hydrolysis. In regard either to conductivity or to ionisation, a substance is less active the more easily it suffers hydrolysis. All the data given in this paper show that non-associated or only slightly associated substances, whether metallic or non-metallic, are hydrolysed or decomposed by water. Referring to metallic compounds only, the alkali chlorides are not appreciably hydrolysed; but metallic tetrachlorides, such as stannic chloride, suffer either complete or very extensive hydrolysis (Bruner, *Zeitsch. physikal. Chem.*, 1900, **32**, 133; Kowalewsky, *Zeitsch. anorg. Chem.*, 1900, **23**, 1; **25**, 189). The result of hydrolysis is, moreover, to transform an electrically inactive into an electrically active substance or substances.

The Cause of the Molecular Association of Salts.

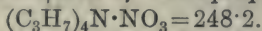
So far it has been demonstrated that the power of forming molecular aggregates rests only with those halogen compounds which are electrically active. Certain considerations suggested that molecular association was not traceable to single elements to which definite residual valencies can, according to modern theories, be assigned; and that substances other than chlorides, bromides, and iodides would be found capable of association in indifferent solvents. The establishment of a connexion between the phenomena of electrolytic dissociation and molecular association necessarily urged this view, to which also certain observations of other workers gave countenance. Thus, Bottomley found that in the fused state

sodium and potassium nitrates are both highly associated (Trans., 1903, **83**, 1422), and Lorenz and Kaufler (*loc. cit.*) have confirmed this discovery. Again, sulphuric acid is highly associated, although the presence of hydroxyl groups has generally been regarded as the cause of association.

In order to test whether salts other than those of the halogens are associated in solution, several such salts have been prepared. Of these, tetrapropylammonium nitrate best fulfilled the required conditions, being easily soluble in chloroform, and being also not very hygroscopic. The following numbers give the result of the test made with this substance.

TABLE X.

Molecular Size in Chloroform of Tetrapropylammonium Nitrate.



Wt. Solute = 1.689 grams.

<i>W</i> (grams).	Δ° .	<i>N</i> .	M. W.	<i>A</i> .
17.74	0.288	38.3	1289	5.2
24.57	0.219	27.7	1224	—
33.02	0.155	20.6	1258	—
39.87	0.136	17.5	1243	5.0

The nitrate is somewhat more associated than the iodide. At a molecular concentration of 25 milligram-molecules per 100 grams of solvent, the association factor (*A*) of the iodide is 4.40, that of the nitrate 5.07. It is of interest to note that among the metallic salts, Bruner (*loc. cit.*) found hydrolysis greater with chlorides than nitrates.

From the results recorded in this paper, including the proof that nitrates are associated, it appears to the author that the theory which considers molecular association as due to the presence of an element of high residual valency is not capable of predicting association, and does very little to explain the cause of association. True it is that in all compounds capable of association there are present elements which may be said to possess unsaturated chemical valencies. The electronegative radicles of salts are composed of such elements. To this extent there is no escape from the theory. But clear demonstration has not yet been made of decided molecular association which can be regarded as due directly to unsaturated elements. Recently it has been shown (Turner and Merry, *loc. cit.*) that the association of tervalent nitrogen compounds only exists when this element is present in distinct electronegative groups; and this condition in at least a considerable measure applies to oxygen compounds. Since also proof exists of the molecular association of acids and of salts, of the association of salts containing

either compound or simple electronegative radicles, it is clear that this association must be assigned to a particular constitution of the substance as a whole. And any theory of the cause of the association must state clearly the function of each of the component parts of the molecule. It is also clear that the association must be due to electrical rather than to the chemical forces such as act between the atoms of a molecule.

So far as electrolytic dissociation is concerned, Abegg (*loc. cit.*) did recognise that the power of ionisation of a salt depended on each component part; and Abegg and Bodländer (*loc. cit.*) stated that an electrochemical theory based on the property of electro-affinity of the component parts of an electrolyte afforded a more satisfactory account of the phenomena of electrolytic dissociation than the chemical valency theory. In this respect their conclusions very largely agree with those to which this paper leads. The difficulty arises, it appears to the author, in attempting to combine the two modes of explanation, electro-affinity and a fixed system of chemical valency.

Two points which are the outcome of this work have a bearing on the theory of electrolytic dissociation, and are very briefly referred to. In the state of vapour, it is known, molecules of salts tend to become simple. In the fused state the complexity is much greater, and increases as the temperature falls. We must suppose, therefore, that marked association exists in the solid state. The various explanations based on the electrolytic dissociation theory of the behaviour of salts in ionising media assume that the molecules which are dissociated into ions are simple (compare Walden, *Zeitsch. physikal. Chem.*, 1907, 59, 209). If, however, the salts before solution in water are associated, and the process of solution is one of simplification, even to the formation of ions, part of the energy changes must be due to a breakdown of the originally associated molecules.

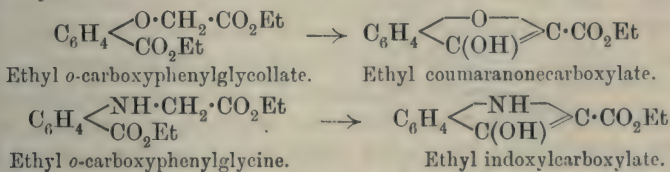
Further, the theory of electrolytic dissociation assumes that electrical forces are called into existence only when ionisation occurs, due to solution in water. The original molecules are considered neutral. But molecular association, due to electrical forces, is so strong in the case of salts that it is not easy to see how the molecules can be regarded as neutral.

The author desires to express his thanks to the Government Grant Committee of the Royal Society for a grant which defrayed part of the cost of this investigation.

XCVI.—*Coumaranone Derivatives. Part I.*

By RICHARD WILLIAM MERRIMAN, M.A.

KETOCOUMARAN or coumaranone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \end{array} \text{CH}$, the "oxygen" analogue of indoxyl, was first obtained by Friedländer and Neudörfer (*Ber.*, 1897, **30**, 1081) by internal condensation of acetoxyacetophenone bromide, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2\text{Br}$. A more convenient source was found by Friedländer in the corresponding monocarboxylic acid, the ester of which was prepared by a similar condensation from ethyl *o*-carboxyphenylglycollate (*Ber.*, 1899, **32**, 1868). This condensation, it should be remarked, is exactly parallel to that of ethyl indoxylcarboxylate from ethyl phenylglycine-carboxylate:



The author having had occasion to prepare considerable quantities of the coumaranonecarboxylic ester, has obtained from it some derivatives which may throw light on the constitution of compounds of this type. Incidentally, ethyl *o*-carboxyphenylglycollate, the parent substance of the coumaranone ester, has for the first time been obtained, with good yield, from accessible materials, and in a pure state.

EXPERIMENTAL.

Ethyl o-Carboxyphenylglycollate and its Monoamide.

Ethyl *o*-carboxyphenylglycollate, which was obtained by Rössing (*Ber.*, 1884, **17**, 2995) in an impure state by esterification of the corresponding acid, is readily prepared directly by condensing ethyl salicylate with ethyl monochloroacetate by means of alcoholic sodium ethoxide. The mixed esters (salicylate, 65 grams; chloroacetate, 50 grams) are added to the sodium ethoxide (sodium, 9 grams in absolute alcohol), and the whole is boiled under a reflux condenser on a water-bath until the product is nearly neutral. This may take over twelve hours, the mixture becoming bright red. After removing the solvent over a water-bath, the product is rendered alkaline with dilute aqueous sodium hydroxide, and repeatedly extracted with ether. The oil which remains after

removing the ether is then fractionated under 20 mm. pressure, on refractionating the portion collected between 185° and 200°, ethyl *o*-carboxyphenylglycollate is obtained as a heavy, colourless oil, which boils at 190—193°/25 mm. The yield is about 45 per cent. of that required by theory:

0.2182 gave 0.4945 CO₂ and 0.1252 H₂O. C=61.8; H=6.4.

C₁₃H₁₆O₅ requires C=61.9; H=6.3 per cent.

By heating this ester with alcoholic ammonia at 100° in sealed tubes, the diamide of *o*-carboxyphenylglycollic acid was obtained by Rössing (*loc. cit.*) as a bright yellow solid. At the ordinary temperature, however, the author finds that a *monoamide* is formed. This is at once precipitated on adding the ester to alcoholic ammonia, the simultaneous formation of a certain amount of the diamide being indicated by the yellowish colour of the mother liquor. It is also obtained, although somewhat more slowly, by the action of either cold concentrated, or hot dilute, aqueous ammonia on the ester. The ester is readily soluble in concentrated ammonia at the ordinary temperature, and in the course of twelve hours the solution deposits a copious precipitate of the monoamide, the presence of some diamide in the mother liquor being again indicated by the colour. With dilute aqueous ammonia, solution is only complete after boiling for twenty minutes, but on then cooling the monoamide is again at once deposited.

The monoamide prepared in any of these ways is simply washed with water and recrystallised from alcohol. It forms colourless needles, and melts at 165° (corr.):

0.1336 gave 7.6 c.c. N₂ (moist) at 18° and 772 mm. N=6.4.

C₁₁H₁₃O₄N requires N=6.3 per cent.

Metallic Derivatives of Ethyl Coumaranonecarboxylate.

The ethyl coumaranonecarboxylate was prepared from ethyl *o*-carboxyphenylglycollate according to Friedländer's directions (*Ber.*, 1899, **32**, 1868); it formed colourless needles, and melted at 66°. Like the corresponding indoxylcarboxylate, it is extremely resistant to hydrolytic agents. In fact, after heating a quantity with excess of 45 per cent. aqueous potassium hydroxide for two hours at 100° (Friedländer, *loc. cit.*), the author found that when the acidified and presumably hydrolysed product was distilled in a current of steam, the ester was recovered unchanged, not a trace of the acid described by Friedländer as resulting from this operation being formed. The recovered ester when recrystallised from alcohol formed the characteristic colourless needles, melting at 66°. (Found, C=64.1; H=5.0. Calc., C=64.1; H=4.9 per cent.)

This very marked resistance to hydrolysis may perhaps be due to the acidic character of the ester, which was established by its conversion into various quite stable, well characterised metallic derivatives.

The *sodium* derivative may be prepared either by adding metallic sodium to a dry ethereal solution of the ester, when hydrogen is evolved and the salt deposited; or by adding the ethereal solution to the calculated amount of sodium ethoxide in alcohol, and at once diluting with dry ether. In either case the precipitate is at once collected, washed with dry ether, and dried in a vacuum at the ordinary temperature, as it darkens at 100° :

0.3403 gave 0.1050 Na_2SO_4 . $\text{Na}=10.0$.

$\text{C}_{11}\text{H}_9\text{O}_4\text{Na}$ requires $\text{Na}=10.1$ per cent.

The *lead* derivative is precipitated as a white powder on adding lead acetate solution to an aqueous solution of the sodium derivative. Like lead malate, it partly melts when boiled with water:

0.2130 gave 0.1042 PbSO_4 . $\text{Pb}=33.4$.

$(\text{C}_{11}\text{H}_9\text{O}_4)_2\text{Pb}$ requires $\text{Pb}=33.5$ per cent.

The *silver* derivative is similarly precipitated as a yellow, gelatinous mass, which, however, at once undergoes decomposition, even in the dark, with formation of metallic silver.

The *ferric* derivative is prepared by adding the theoretical amount of an ethereal solution of anhydrous ferric chloride to an ethereal solution of the dry ester. A blue colour is at once developed. After a time the excess of ferric chloride is removed by repeatedly shaking with cold water, the solution being afterwards freed from drops of water by filtering through a dry filter. The salt is then precipitated by adding light petroleum. It forms deep blue nodules, is readily soluble in alcohol or ether, but insoluble in water, light petroleum, or benzene. For analysis it was dried at 100° :

0.1853 gave, on ignition, 0.0215 Fe_2O_3 . $\text{Fe}=8.1$.

$(\text{C}_{11}\text{H}_9\text{O}_4)_3\text{Fe}$ requires $\text{Fe}=8.3$ per cent.

The formation of these well-defined and stable metallic derivatives, and the intensely blue colour of the ferric compound would seem to indicate that ethyl coumaranonecarboxylate is constituted in a similar manner to the corresponding indoxylcarboxylate, namely, as an enolic compound. The constitution of the sodium derivative, at all events, must certainly be represented by the formula $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}(\text{ONa}) \end{array} \text{C} \cdot \text{CO}_2\text{Et}$, unless, indeed, it be admitted that owing to the juxtaposition of two carbonyl groups the hydrogen of the methenyl group present in the ketone modification may

function as acidic. This alternative, however, would not account for the intense and characteristic colour of the ferric compound.

Phenylhydrazine and Azo-derivatives of Coumaranonecarboxylic Acid.

Although the metallic derivatives of ethyl coumaranonecarboxylate are undoubtedly enolic in constitution, the ester itself reacts with phenylhydrazine in the normal ketonic manner, and it is quite clear, therefore, that its nucleus is ketonic. The first product of the interaction, however, is neither a hydrazide nor a hydrazone, but an azo-compound resulting apparently from the oxidation of the hydrazide.

When ethyl coumaranonecarboxylate is mixed with a molecular proportion of phenylhydrazine in alcoholic solution, there is no obvious action at the outset. In the course of a day, however, a red colour develops, and in two days a substance begins to be deposited in yellowish plates, which a week later may be separated. After washing with a little cold alcohol, the product is purified by dissolving in dilute ammonia, and reprecipitating with dilute hydrochloric acid. Finally it is washed with cold water, and recrystallised from boiling alcohol, in which it is moderately soluble.

Benzeneazocarbonylcoumaranone, $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{CH} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$, forms well-defined, orange needles, melts at $182\text{--}183^\circ$, and slowly decomposes at 200° , with evolution of nitrogen. With the exception of benzene and boiling alcohol it is but sparingly soluble in the usual organic solvents. For analysis it was dried at 100° :

0.2042 gave 0.5065 CO_2 and 0.0706 H_2O . $\text{C}=67.6$; $\text{H}=3.8$.

0.1569 „ 0.3882 CO_2 „ 0.0556 H_2O . $\text{C}=67.5$; $\text{H}=3.9$.

0.2247 „ 20.0 c.c. N_2 at 14° and 761 mm. $\text{N}=10.5$.

The molecular weight in alcoholic solution was determined by Landsberger's method:

0.2865 in 22.56 alcohol gave $\text{E}=0.054$. $\text{M.W.}=271$.

0.2750 „ 22.77 „ „ $\text{E}=0.052$. $\text{M.W.}=275$.

$\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}_2$ requires $\text{C}=67.7$; $\text{H}=3.8$; $\text{N}=10.5$ per cent.
 $\text{M.W.}=266$.

This curious azo-compound is unique, the only known substance at all approaching it in type being Fischer's benzoylazobenzene, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_5$ (*Annalen*, 1877, **190**, 126), which, however, is essentially different in properties. Although neutral to litmus, the coumaranone derivative is freely soluble in dilute ammonia; it is quite stable towards boiling aqueous potassium hydroxide or concentrated hydrochloric acid.

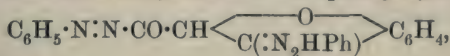
The *silver* derivative, the formation of which serves to confirm the potentially enolic character of the coumaranone nucleus, is readily precipitated by silver nitrate from a solution of the azo-compound in the minimal amount of ammonia. It forms a brick-red powder, which, after washing successively with alcohol and water and drying in a vacuum, melts at 241° , but at the same time begins to decompose:

0.1760 gave, on ignition, 0.0520 Ag. Ag=29.5.

$C_{15}H_9O_3N_2Ag$ requires Ag=29.0 per cent.

When, however, a large excess of phenylhydrazine is added to the alcoholic solution of the coumaranone ester, or the hydrazine is added to an alcoholic solution of the azo-compound, a new product is slowly precipitated in splendid red needles. It may be washed with cold alcohol, and recrystallised from boiling alcohol, in which it is only sparingly soluble. It is readily soluble in benzene or pyridine.

Benzeneazocarbonylcoumaranonephenylhydrazone,



forms fine, ruby-red needles, and melts at 193° (corr.). For analysis it was dried at 100° :

0.2152 gave 0.5548 CO_2 and 0.0876 H_2O . C=70.3; H=4.5.

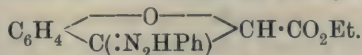
0.2017 „ 0.5214 CO_2 „ 0.0820 H_2O . C=70.5; H=4.5.

0.2040 „ 27.2 c.c. N_2 (moist) at 15° and 763 mm. N=15.7.

$C_{21}H_{16}O_2N_4$ requires C=70.8; H=4.5; N=15.7 per cent.

Unlike its precursor, this substance is quite insoluble in ammonia, and hence certainly does not contain an enolic group or any other group capable of showing an acidic function. When boiled with concentrated aqueous potassium hydroxide it is dissolved, and, to a certain extent, hydrolysed, the odour of phenylhydrazine becoming apparent. On acidifying the solution with hydrochloric acid, the greater part of the hydrazone is recovered unchanged, but a small portion of the product is now soluble in ammonia, and from this ammoniacal solution the original azo-compound is precipitated on acidification. There is no doubt, therefore, that the red compound is, as stated, the phenylhydrazone of the yellow azo-compound.

Ethyl Coumaranonecarboxylate Phenylhydrazone,



As the azo-compound thus behaves as a ketone, it was to be expected that the original ester would also do so, and on one occasion, by the interaction of an alcoholic solution of the ester

with a solution of phenylhydrazine in 50 per cent. acetic acid, a product crystallising in yellow needles was obtained. This was washed with dilute acetic acid and then with water, and recrystallised from dilute alcohol. It forms small, yellow needles, readily soluble in cold alcohol, ether, benzene, or chloroform. It reddens at 105°, and melts at 125–126°:

0.1847 gave 0.4649 CO₂ and 0.0898 H₂O. C=68.7; H=5.4.

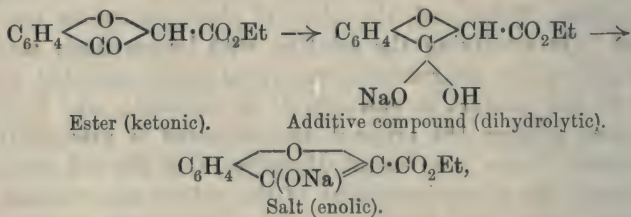
0.1817 „ 14.7 c.c. N₂ (moist) at 17° and 772.5 mm. N=9.4.

C₁₇H₁₆O₃N₂ requires C=68.9; H=5.4; N=9.5 per cent.

The phenylhydrazone reduces boiling Fehling's solution, and readily undergoes normal hydrolysis with alkalis or acids. Its behaviour towards light is similar to that of benzaldehydephenylhydrazone (Chattaway, Trans., 1906, **89**, 462). On being kept in the daylight it gradually reddens, and in five days is quite red. The melting point does not alter. On leaving in the light for several weeks it gradually fades to a dirty buff colour. The melting point is still unchanged. If the substance is now placed in the dark for a week it regains the original yellow colour of the freshly-formed phenylhydrazone, and has the same melting point.

The preparation of this simple hydrazone proved to be an isolated one, and in spite of many subsequent attempts the conditions under which it was formed could never be repeated, the orange azo-compound always being produced.

The dual character of ethyl coumaranonecarboxylate may, of course, be explained by the hypothesis of tautomerism. There is no real need, however, to assume other than the ketonic constitution for the ester itself, as the formation from it of enolic salts may readily be accounted for by the far simpler hypothesis of the formation of an additive compound followed by elimination of water:



This work was commenced at Cambridge at the suggestion of Dr. Ruhemann, to whom I here offer my best thanks: the compounds described in this paper are still being examined, and the work is being extended. An endeavour is also being made to prepare similar azo-compounds from ethyl indoxylcarboxylate.

XCVII.—*The Influence of Temperature on the Basic Water Value of Ethyl Alcohol.*

By WILLIAM JACOB JONES and ARTHUR LAPWORTH.

IT has already been demonstrated that at 25° the availability (or the measure of the salt-forming power) of a highly dilute solution of hydrogen chloride in ethyl alcohol containing small quantities of water may be expressed by the formula $P = c \cdot \frac{K}{r + w}$, where P is the availability, c is the concentration of the hydrogen chloride, K is an arbitrary constant, w is the concentration of the water, and r is the basic "water value" of absolute alcohol at 25°. Further, that at this temperature the catalytic activity of the hydrogen chloride in such solutions, as measured by the velocity of esterification of monobasic carboxylic acids, is proportional to its availability, so that the velocity of esterification in this solvent may be represented by the differential equation:

$$-\frac{dy}{dt} = k \cdot y \cdot P,$$

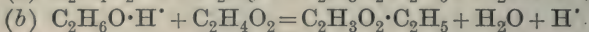
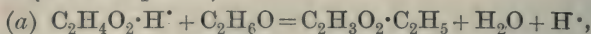
where k is a constant, and y the concentration of the carboxylic acid. Combining the two foregoing expressions, the equation:

$$-\frac{dy}{dt} = \frac{kyc}{r + w},$$

which is identical, except for the symbols chosen, with an equation which had previously been used by Goldschmidt and Udby (*Zeitsch. physikal. Chem.*, 1907, **60**, 728 *et seq.*). These authors, however, had arrived at it by assuming that esterification, when brought about by the catalytic agency of a mineral acid, involves a reaction between the molecule of the carboxylic acid and a complex alcohol-hydrion, $C_2H_5O \cdot H'$, and adduced the fact that the reaction does progress in accordance with this equation as evidence against an alternative view of esterification mechanism. It has since been pointed out on several occasions that such a point of view is not a tenable one, as both hypotheses lead to the same equation, and this result has not since been directly assailed. Recently, however, Goldschmidt has declared that this criticism was not a valid one (*Zeitsch. physikal. Chem.*, 1910, **70**, 628, footnote 2), and therefore it has become necessary to submit the views propounded by this distinguished chemist and his colleague to a somewhat detailed analysis.

These authors proceed by discussing two alternative hypotheses as to the course of esterification of acetic acid in presence of an

acid catalyst in alcoholic solution. These hypotheses are expressed as follows (*loc. cit.*, p. 729):



In discussing the possibility that the reaction proceeds in accordance with (a) (the hypothesis which is finally rejected), the following symbols are used. The initial concentration of the carboxylic acid is a , and $a-x$ is its concentration at the time t from the beginning of esterification; b is the concentration of the alcohol, c that of the acid acting as catalyst,* and ξ is the concentration of the complex ion ($\text{C}_2\text{H}_4\text{O}_2 \cdot \text{H}^+$).

The velocity of the reaction is then given by the equation:

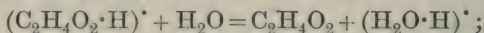
$$\frac{dx}{dt} = k b \cdot \xi \quad \text{(equation 1, p. 729),}$$

k being the "velocity constant."

The relation between ξ , $a-x$, and c is expressed:

$$\xi = \kappa c(a-x-\xi) \quad (2),$$

where κ is a new equilibrium constant. This relation, it is pointed out (p. 731), holds true only in absolute alcohol, and therefore at the first instant of the esterification process, for the water produced instantly reacts as follows:



and consequently the value of ξ is diminished by a certain amount η .

So far, no exception can be taken to the reasoning, but the proposition which is next introduced shows clearly that these authors were very far from forming a true conception of the state of equilibrium between acids, bases, and solvent, and fully accounts for their erroneous view that the carriers of catalytic activity of acids are the complexes formed by the hydrogen ions with the solvent.

Briefly stated, the proposition referred to is as follows: *If the concentration of the $\text{H}_2\text{O} \cdot \text{H}^+$ ions formed is represented by η , then η also represents the decrease in the value of ξ .* In other words, the complex $\text{H}_2\text{O} \cdot \text{H}^+$ ions are formed wholly at the expense of the $\text{C}_2\text{H}_4\text{O}_2 \cdot \text{H}^+$ ions (*loc. cit.*, p. 731).

Similarly, if the esterification proceeds in accordance with the equation (b) given above, these authors assume that the $\text{H}_2\text{O} \cdot \text{H}^+$ ions are formed exclusively at the expense of the $\text{C}_2\text{H}_6\text{O} \cdot \text{H}^+$ ions.

In general terms, therefore, these authors argue that the $\text{H}_2\text{O} \cdot \text{H}^+$ ions are formed exclusively at the expense of those parti-

* Later (p. 732), it is pointed out that c is more accurately the concentration of the electrolytically dissociated part of the acid which serves as catalyst, and this is assumed to be constant as is nearly the case in highly dilute solution.

cular ions which are directly concerned in the process of esterification as expressed by hypothesis (a) or hypothesis (b) respectively. In point of fact it so happens that the main bulk of the hydrions present during the process of esterification in absolute alcohol are united with the solvent, and, consequently, as the alcohol is a very weak base, the $\text{H}_2\text{O}\cdot\text{H}^+$ ions are formed mainly at the expense of the complex alcohol hydrions. The assumption used by Goldschmidt and Udby may here legitimately be introduced as an approximation in the discussion of hypothesis (b), but not in hypothesis (a). As both hypotheses, correctly treated, lead to the same velocity equations, these authors naturally obtained a correct expression in case (a) and an incorrect one in case (b).

It is quite obvious that if there were initially present two or more kinds of hydrions, simple or complex, in equilibrium with one another, these would each and all have some share, at least, in the production of the new $\text{H}_2\text{O}\cdot\text{H}^+$ ions. Hence the proposition employed by Goldschmidt and Udby requires (i) that the solution contains no appreciable amount of free hydrogen ions,* and (ii) that there are present no appreciable amounts of hydrolysable complex hydrions formed from weak bases other than those which play a direct part in the esterification process. In other words, if hypothesis (a) were correct, then, before the introduction of the water, all the hydrions must be present as $\text{C}_2\text{H}_4\text{O}_2\cdot\text{H}^+$ ions, that is, $c=[\text{C}_2\text{H}_4\text{O}_2\cdot\text{H}^+]$, and, if (b) were correct, then $c=[\text{C}_2\text{H}_6\text{O}\cdot\text{H}^+]$. Now c , the concentration of the active catalyst, is assumed constant throughout, so that the $\text{C}_2\text{H}_4\text{O}_2\cdot\text{H}^+$ ions must be constant in concentration and independent of the total concentration of acetic acid in case (a), and the $\text{C}_2\text{H}_6\text{O}\cdot\text{H}^+$ ions independent of the concentration of alcohol in case (b). The velocity of esterification in case (a) thus becomes:

$$\begin{aligned} & k[\text{C}_2\text{H}_4\text{O}_2\cdot\text{H}^+] \times [\text{C}_2\text{H}_6\text{O}] \\ & = kc[\text{C}_2\text{H}_6\text{O}], \end{aligned}$$

which is independent of the concentration of the acetic acid; in case (b) it becomes:

$$\begin{aligned} & k[\text{C}_2\text{H}_6\text{O}\cdot\text{H}^+] \times [\text{C}_2\text{H}_4\text{O}_2] \\ & = kc[\text{C}_2\text{H}_4\text{O}_2], \end{aligned}$$

which is independent of the concentration of the alcohol.†

It is, of course, not permissible to proceed as did Goldschmidt and Udby, namely, to discuss the influence of water upon the

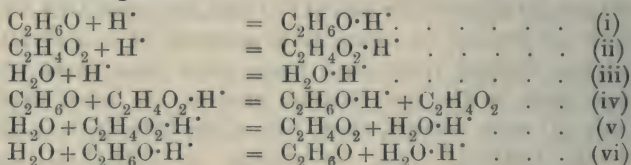
* On page 755 (*loc. cit.*), the presence of free hydrogen ions is, nevertheless, referred to as certain.

† This deduction (Trans., 1908, **93**, 2169) has been alluded to by Goldschmidt (*Zeitsch. physikal. Chem.*, 1910, **70**, 628, footnote) as due to a misunderstanding. The fallacy, of course, lies in the view for which he and his colleague were responsible.

concentration of the $C_2H_4O_2 \cdot H^+$ ions, without considering at the same time the rôle of the solvent alcohol. If due regard is paid to this, it is legitimate to argue as follows.

Small quantities of compounds, such as weak carboxylic acids or esters, influence the properties of an alcoholic solution of a mineral acid only to a very small extent; hence, their basic affinities cannot be appreciably greater than that of alcohol, and are probably, as a rule, smaller. Assuming, as the earlier authors did, that the hydriions in an alcoholic solution of hydrogen chloride are partly free (as H^+) and partly united with the solvent (say, as $C_2H_6O \cdot H^+$), the equilibrium conditions in such a solution are very easily expressed if the law of mass action holds good.

Adopting the general line followed by Goldschmidt and Udby in discussing hypothesis (a) up to the point where the influence of water on the concentration of $C_2H_4O_2 \cdot H^+$ or ξ is considered, the instantaneous equilibria to be dealt with may be expressed in the following chemical equations:



Only three of these are independent equations, and only three independent constants are therefore necessary to define the instantaneous equilibrium between all the components.

For the sake of clearness, the concentrations may be represented by letters corresponding with those used by Goldschmidt and Udby, or, in full, by bracketing the chemical symbol for the component referred to. The law of mass-action would thus give the following relations:

$$\frac{\xi_1^*}{h} = \frac{[C_2H_6O \cdot H^+]}{[H^+]} = K_1[C_2H_6O] \equiv K_1b \quad \dots \quad (vii)$$

$$\frac{\xi_2}{h} = \frac{[C_2H_4O_2 \cdot H^+]}{[H^+]} = K_2[C_2H_4O_2] \equiv K_2(a-x) \quad \dots \quad (viii)$$

whence:
$$\frac{\xi_1}{\xi_2} = \frac{[C_2H_6O \cdot H^+]}{[C_2H_4O_2 \cdot H^+]} = \frac{K_1[C_2H_6O]}{K_2[C_2H_4O_2]} = \frac{K_1b}{K_2(a-x)} \quad \dots \quad (ix)$$

The quantities b and $(a-x)$ are supposed to be practically unaffected by the presence of small quantities of water, which is apparently nearly true.† Hence from equations vii, viii, and ix the

* Goldschmidt and Udby use ξ to express the concentration of the $C_2H_6O \cdot H^+$ ion in one place and the $C_2H_4O_2 \cdot H^+$ ion in another; to avoid confusion, the symbols ξ_1 and ξ_2 are here used throughout.

† The experiments described in the present paper and a previous one make

ratios of ξ_1 , ξ_2 , and h must also be independent of the amount of water present (within the limits where the solution is one in which the law of mass action applies). In other words, when water is added, or formed within the system, and forms $\text{H}_2\text{O}\cdot\text{H}'$ ions, the ratios of ξ_1 , ξ_2 , and h are unaltered, or the same fraction of each disappears. This may be expressed by saying that the availability of the acid is diminished by a definite amount, and the ratio of the new availability to the old is measured by the ratio of the new to the old value of any one of the quantities ξ_1 , ξ_2 , or h . Obviously the increase in the value of η must be equated, not to the diminution in $[\text{C}_2\text{H}_4\text{O}_2\cdot\text{H}']$, as was done by Goldschmidt and Udby, but to the total diminution in $\xi_1 + \xi_2 + h$.

It is unnecessary to proceed further with the development of separate equations for the velocity of esterification corresponding with the hypotheses (a) and (b) respectively, as the following very elementary consideration shows.

At any moment during the course of the reaction the equilibrium corresponding with equation (iv) above obtains, hence:

$$[\text{C}_2\text{H}_6\text{O}][\text{C}_2\text{H}_4\text{O}_2\cdot\text{H}'] = K_4[\text{C}_2\text{H}_6\text{O}\cdot\text{H}'][\text{C}_2\text{H}_4\text{O}_2] \quad \dots \quad (\text{x}),$$

where K_4 is a constant at any fixed temperature and in any given medium.

The velocity of the reaction expressed by hypothesis (a) is given by:

$$\frac{dx}{dt} = k_1[\text{C}_2\text{H}_6\text{O}][\text{C}_2\text{H}_4\text{O}_2\cdot\text{H}'] \quad \dots \quad (\text{xi})$$

while hypothesis (b) leads to the expression:

$$\frac{dx}{dt} = k_2[\text{C}_2\text{H}_6\text{O}\cdot\text{H}'][\text{C}_2\text{H}_4\text{O}_2] \quad \dots \quad (\text{xii})$$

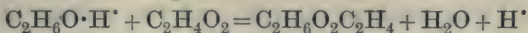
but by (x) equation (xi) for hypothesis (a) may also be written:

$$\frac{dx}{dt} = k_1 K_4[\text{C}_2\text{H}_6\text{O}\cdot\text{H}'][\text{C}_2\text{H}_4\text{O}_2] = k_3[\text{C}_2\text{H}_6\text{O}\cdot\text{H}'][\text{C}_2\text{H}_4\text{O}_2],$$

identical in form with that given by hypothesis (b).

That is, hypotheses (a) and (b) cannot possibly lead to velocity equations of different types if the law of mass-action holds good.

Recently Goldschmidt has departed somewhat from his former point of view that the equation



represents the stage in esterification which proceeds within measurable speed; he now adopts the view that the measured velocity is that of the breaking down of a complex ion, $\text{C}_2\text{H}_6\text{O}\cdot\text{C}_2\text{H}_4\text{O}_2\cdot\text{H}'$. This,

it certain that in dilute solution water acts almost wholly by influencing the catalyst or its combinations, and does not appreciably affect the active mass of the alcohol or the carboxylic acid.

again, leads to the same velocity equations. It is not the object of the present communication, however, to select any one of these three hypotheses, but to show beyond doubt that they do not admit of being distinguished from one another by arguments based on the velocity of catalytically-accelerated esterification, and that for all three cases the velocity must be represented by an equation of the form - $\frac{dy}{dt} = kyP$, explained at the beginning of this paper.

In the expression $P = c \cdot \frac{K}{r+w}$ for the availability of a mineral acid, w represents the concentration of the free water, but when the concentrations of the water and mineral acid are comparable an appreciable portion of the water present may be rendered inactive by forming complexes with the catalyst.

Goldschmidt and Udby developed a formula for the velocity of esterification, in which the influence of the catalyst on the concentration of the water was allowed for, the assumption being made that the fall in the concentration of the water was due solely to the formation of ions of the formula $H_2O \cdot H^+$, but the measurements made by them were not in the best accordance with the resulting equation, and the present authors venture to suggest that the chloridions may also unite with part of the water. For reasons such as these it is hardly possible at present to calculate a priori the correction which must be made in the value of w when its magnitude approaches that of c .

Fortunately, however, if c is considerably smaller than r , the value of $r+w$, calculated on the assumption that all the water is free, will probably be affected by the foregoing consideration so little that during experiments such as those described in the present paper its influence can be felt only in the initial stages of esterification, and will not be greater than the errors at present inherent in the methods of measurement.

The practical work described in the present paper is an extension of the experiments described by Lapworth and Partington (Trans., 1910, **97**, 19). The latter were able to show that at 25° the velocity of esterification of phenylacetic acid in ethyl alcohol is within the limits of experimental error proportional to the availability of the hydrogen chloride used as catalyst, and the present authors have now ascertained that this is equally true at any temperature between 0° and 25° .

Goldschmidt and Udby (*Zeitsch. Elektrochem.*, 1909, **15**, 7 and 8) found that the value of r fell from 0.15 at 25° to 0.095 at 0° ; the results described in the present communication are qualitatively of the same general character, but, as was pointed out in a previous

paper, the concentration of catalyst used affects the apparent values of r very considerably, and the measurements detailed here were carried out with mineral acids having low concentrations.

As the influence of water is nearly twice as great at 0° as at 25° , and varies in the same manner, whether measured by means of experiments on esterification or by observations on the affinity of hydrogen chloride for a dissolved weak base, the intimate connexion between the catalytic activity and availability of highly ionised hydrogen chloride in alcohol can no longer be a matter of doubt. In conjunction with the work of Arrhenius, Ostwald, and their followers on the behaviour of acids in aqueous solution, and with the work of Goldschmidt and his pupils on the relation between catalytic activity and conductivities of acids in alcoholic solution, it is safe to surmise that in such solvents the catalytic activity of a very highly ionised acid is nearly proportional to its availability, and that the presence of other substances in the solvent will not usually affect this relationship providing that these substances are present in such quantities that the solution can reasonably be regarded as a "dilute" one. In some cases there is reason to believe that a rough proportionality holds over a very wide range.

EXPERIMENTAL.

The measurements of the velocity of esterification of phenylacetic acid were made in the manner described by Lapworth and Partington (*Trans.*, 1901, **97**, 29 *et seq.*), the temperature of the thermostat varying in different experiments between 0° and 25° .

The change in the availability of the hydrogen chloride with varying quantities of water was determined as before by measurements of the acidity of the solutions, as shown by the alteration in tint of a minute quantity of dissolved weakly basic indicator, but while some of these estimations here recorded were carried out in the manner previously described, the majority were made by employing a spectrophotometer.

The advantages which attached to the use of the latter were numerous, and in particular it was found less difficult to carry out experiments with solutions at any desired temperature than was the case with the ordinary tintometer, and the liquids were subject to less exposure to the atmosphere than in the latter instance, and a serious source of error minimised. The liquid under examination was enclosed in a bottle in the form of a cube, constructed with plate-glass sides, closely cemented together at the edges, one side being pierced and cemented to a tube of about half-inch diameter, which served as the neck through which the cube could be filled and emptied. The joints were rendered impervious to water and

to alcohol by covering them repeatedly with a solution of india-rubber in chloroform and allowing the solvent to evaporate slowly. In order to ensure that the materials would not affect the availability of the acid, the cube was filled with a concentrated solution of hydrogen chloride in absolute alcohol, and allowed to remain for several weeks, then washed out repeatedly with absolute alcohol. After this treatment it was found that the tint of highly dilute alcoholic solutions of hydrogen chloride coloured with an indicator was not appreciably affected by remaining in this cube for eighteen hours, even when the cube was kept fully immersed in water.

During measurements made with the spectrophotometer, the hollow cube was immersed in water contained in an oblong trough, the longer sides of which consisted of parallel glass plates about six inches apart and the ends and the bottom of thin metal. The contents of this trough were kept at the desired temperature usually by means of a small flame automatically adjusted by a thermostat contained in the trough, and when the desired temperature was below that of the room, ice-water or ice was added in the usual manner to the liquid in the trough; in this way a temperature which did not vary by more than 0.5° during the course of a series of measurements could be maintained. A greater accuracy than this was not found necessary, as a change of even one degree made no very perceptible difference to the tints of the solutions used.

The spectrophotometer used was one in which the amount of light passing through the two comparison tubes is altered at will by varying the size of the slits on which the light fell, this being effected by the rotation of screens provided with scales on which alterations in the breadth of the slits could be read off. In making measurements, the instrument was placed in a fixed position with the receiving tubes at right angles to the glass sides of the thermostat, the upper tube being opposite the centre of the immersed cube; the latter was raised on three small washers above the floor of the trough, and was readjusted after each reading by turning it by hand through 90° and replaced once more, so as to present the centre of the original face to the tube of the spectrophotometer and with the plane of its face, as nearly as could be judged by the eye, at right angles to that tube. In this way errors due to imperfect adjustment were in the mean virtually eliminated. The upper tube of the instrument received the light which had passed through the cube, whilst the lower tube received light directly from the lamp, being below the level of the thermostat. A sensitive portion of the spectrum in the blue-green region was selected where only the salt of the indicator showed appreciable absorption.

The alcoholic hydrogen chloride or water was added from a

standard burette (reading directly to 0.01 c.c.), and, without removing the cube from the bath, thorough admixture was ensured by shaking before further readings were taken. The alcoholic hydrogen chloride used contained in all cases the same concentration of indicator as the liquid in the cube, and as the amount of water added was always too small to affect appreciably the total bulk of liquid, the concentration of the indicator during any series of measurements was always constant within the limits of experimental error. The source of light used was a Nernst lamp at a distance of 6 feet from the thermostat.

The width of the slit receiving light which had passed through the cube was kept constant in all measurements recorded, and equality of intensity of the two halves of the field seen at the eyepiece was obtained by altering the size of the slit directly illuminated by the lamp.

From a series of measurements it was found that if S_0 was the width of the adjustable slit as read off on the scale when no hydrogen chloride was present, S was the apparent width of this slit when the hydrogen chloride in the alcohol had the concentration c , k' being a constant; then the formula $\log \frac{S_0}{S} = k'c$ applied satisfactorily when

the value of S was not greater than 90 scale divisions, but a constant discrepancy was observed when S was small, and this was attributed to a displacement of the zero of the scale; a value for the zero was therefore chosen by trial, which led to uniform concordance with the above formula. The displacement was small, namely, 1.2 divisions of the scale, or 0.015 mm., and did not vary appreciably during the whole series of measurements. The actual breadth of the adjustable slit never exceeded 60 scale divisions, and in most cases S_0 (corrected) was 58.8 (or 0.735 mm.), the width of the upper slit corresponding with this being determined before each experiment.

The following measurements made with varying concentrations of hydrogen chloride in a sample of absolute alcohol will serve to show that the logarithmic law holds good with the conditions adopted. The concentration of *p*-tolueneazodiphenylamine was 1 gram in 100,000 c.c. of liquid.

Experiment I.—Temperature 25°.

In column H is given the total volume of added alcoholic HCl (between 0.1 and 0.03*N*) present.

In column V the total volume of alcoholic in the cube.

In column C the concentration of the acid in the solution, or $\frac{100H}{V}$.

In column *S* the corrected width of slit in small scale units.

In column *L* the logarithm of $\frac{S_0}{S}$.

In column *Z* the value of $\frac{L}{C}$.

<i>H.</i>	<i>V.</i> [*]	<i>C.</i>	<i>S.</i>	<i>L.</i>	<i>Z.</i>
0	50.00	—	58.8	—	—
0.45	50.45	0.892	44.1	0.1250	0.140
0.96	50.96	1.884	30.8	0.2808	0.150
1.38	51.38	2.686	24.8	0.3749	0.140
1.79	51.79	3.456	19.2	0.4861	0.141
2.59	52.59	4.925	10.85	0.7339	0.149
3.04	53.04	5.732	9.05	0.8128	0.142
4.42	54.42	8.121	4.04	1.1630	0.143

Experiment II.—Temperature 16°.

(The alcoholic hydrogen chloride was different from that used in experiment I.)

<i>H.</i>	<i>V.</i>	<i>S.</i>	<i>Z.</i>
0	50.00	58.8	—
0.65	50.65	43.4	0.103
0.90	50.90	39.1	0.100
1.52	51.52	29.6	0.110
1.84	51.84	27.1	0.095
2.90	52.90	15.8	0.104
3.46	53.46	13.5	0.099
4.87	54.87	7.44	0.101
5.60	55.60	6.70	0.094

The approximate constancy in the values for *Z* indicate that the logarithmic formula is nearly applicable, and show that the separate measurements were affected by considerable experimental errors. With experience in the manipulation more concordant readings might possibly be obtained.

Determination of the Water Value of a Sample of Alcohol.

The alcohol was prepared for examination by using a portion of it for the preparation of a solution of *p*-tolueneazodiphenylamine of the strength already stated; 1 c.c. of this solution was placed in a 50 c.c. delivering flask, which was filled to the mark with the pure liquid, and the contents transferred to the cube. Measurements were made as previously described, but hydrogen chloride gas, admitted by a small jet, was used instead of an alcoholic solution, and successive small quantities of water were then added, and the influence of these on the tint of the solution determined.

In the following tables no allowance for the alteration in volume produced by the water was made, as its effect was within the limits of experimental error.

In column IV is given the total volume of water added; *S* and *L*

have the meanings indicated above. From these, R , or the water value (in grams of water) of the 50 c.c. of alcohol, was determined by a graphic method, and the value of $R + W$, the total estimated basic water value in grams of the liquid in the cube, is given in the column under that heading. Column Z gives the corresponding value for $(R + W) \times L$.

V is the volume of alcohol used, and r is water value of a litre of the sample of alcohol in gram-equivalents, or

$$r = \frac{1000R}{18V}.$$

The value of S_0 was 58.8 in all the cases cited below, and the concentration of hydrogen chloride nearly $N/1000$, but the amount to be used was judged merely by the production of a suitable colour in the solution.

Experiment I.—Alcohol not quite anhydrous.

Temperature = 25° . $V = 54.4$. ($R = 0.105$. $r = 0.107$.)

W .	S .	L .	$R + W$.	Z .
0.00	4.04	1.1630	0.105	0.122
0.12	16.6	0.5493	0.225	0.124
0.20	23.8	0.3928	0.305	0.120
0.30	30.5	0.2851	0.405	0.115
0.45	35.7	0.2167	0.555	0.120

Experiment II.—In all the following cases anhydrous alcohol was used, and V was 50.

Temperature = 25° . ($R = 0.085$. $r = 0.094$.)

W .	S .	L .	$R + W$.	Z .
0.00	5.8	1.0060	0.085	0.084
0.13	23.3	0.4020	0.215	0.086
0.20	29.0	0.3070	0.285	0.087
0.30	31.6	0.2697	0.385	0.083
0.40	39.2	0.1761	0.485	0.085
0.50	42.4	0.1420	0.585	0.085

Experiment III.—Temperature = 1° .

($R = 0.049$. $r = 0.055$.)

W .	S .	L .	$R + W$.	Z .
0.00	5.91	0.9978	0.049	0.049
0.10	28.2	0.3192	0.149	0.048
0.15	33.1	0.2496	0.199	0.050
0.20	38.3	0.1862	0.249	0.046
0.25	41.1	0.1556	0.299	0.047

Experiment IV.—Temperature=12°.

$$(R=0.070. \quad r=0.080.)$$

<i>W.</i>	<i>S.</i>	<i>L.</i>	<i>R + W.</i>	<i>Z.</i>
0.00	5.53	1.0267	0.070	0.072
0.10	22.2	0.4230	0.170	0.072
0.15	27.8	0.3254	0.220	0.072
0.25	35.8	0.2155	0.320	0.069
0.35	40.2	0.1652	0.420	0.069
0.45	43.0	0.1359	0.520	0.071

All the values for r determined by the foregoing method are given in the table at the end of this paper.

Esterification Experiments.

These experiments and the calculations associated with them were made in the manner previously described (Trans., 1910, **97**, 29). The numbers in the columns headed T refer to the time, in minutes from the commencement of reaction, and in those headed y are given the corresponding titres of 10 c.c. of the solution in terms of $N/10$ -alkali, the necessary correction for the hydrogen chloride present having been made. The values of kc calculated for different values of r are given, and the values of y for $T=0$ are those calculated by graphic extrapolation of the values of $\log y$.

SERIES I.—Temperature 25°.

Concentration of HCl, 0.0170*N*.

Flask I: Volume=50.18 c.c. No water initially present.

<i>T.</i>	<i>y.</i>	<i>k.c.* × 10⁴</i>		
		$r=0.09$	0.10	0.11
[0.0	20.04]	—	—	—
7.0	19.33	—	—	—
22.0	17.80	—	—	—
59.0	15.10	5.68	6.14	6.62
104.0	12.58	5.90	6.35	6.79
171.5	10.10	5.82	6.22	6.61
251.0	7.95	5.92	6.28	6.50
333.0	6.35	5.94	6.28	6.62
Mean.....		5.85	6.25	6.65

* The values given for series *A*, *B*, *C*, in a former paper (Trans., 1910, **97**, 30—32) were those for $10^4.k.c.$, and not $k.c.$ as stated, and for series *D*, *E* those for $10^3.k.c.$, and not $k.c.$

Flask II: Volume=50.17. Water=0.200 gram initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴</i>		
		<i>r</i> =0.09	0.10	0.11
[0.0	19.12	—	—	—
7.5	18.91	—	—	—
17.0	18.62	—	—	—
50.0	17.62	—	—	—
147.0	14.74	6.00	6.15	6.35
240.5	12.68	5.97	6.14	6.31
351.5	10.67	5.97	6.14	6.31
Mean.....		5.98	6.14	6.32

The value of *r* was evidently about 0.095.

SERIES II.—Temperature 18°.

Concentration of HCl, 0.0171*N*.

Flask I: Volume 50.18 c.c. No water initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴</i>		
		<i>r</i> =0.07	0.09	0.12
[0.0	30.29]	—	—	—
11.5	29.19	—	—	—
23.7	28.02	—	—	—
79.5	24.10	—	—	—
145.5	21.04	3.03	3.52	4.26
232.0	18.08	3.06	3.49	4.14
321.5	15.62	3.15	3.56	4.17
432.0	13.28	3.20	3.57	4.14
567.0	11.17	3.20	3.55	4.06
Mean		3.13	3.55	4.15

Flask II: Volume 50.16 c.c. Water=0.200 gram initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴</i>		
		<i>r</i> =0.07	0.09	0.12
[0.0	30.41]	—	—	—
12.0	29.92	—	—	—
24.0	29.43	—	—	—
117.0	26.60	—	—	—
289.5	22.52	3.43	3.64	3.95
415.5	20.22	3.28	3.48	3.76
606.5	17.38	3.34	3.60	3.84
Mean		3.35	3.57	3.84

The value of *r* evidently lay close to 0.09.

SERIES III.—Temperature 18°.

Concentration of HCl, 0.0171*N*.

Flask I: Volume 50.18 c.c. No water initially present.

<i>T.</i>	<i>y.</i>	<i>k.c.</i> × 10 ⁴ .		
		<i>r</i> = 0.07	0.09	0.10
[0.0	33.75]	—	—	—
14.7	32.32	—	—	—
25.0	31.19	—	—	—
41.0	29.65	—	—	—
100.5	26.02	—	—	—
217.0	21.42	—	—	—
307.0	18.48	3.06	3.44	3.63
425.5	15.69	3.11	3.47	3.65
548.5	13.46	3.16	3.48	3.65
671.0	11.73	3.16	3.47	3.62
Mean		3.13	3.47	3.64

Flask II: Volume 50.17 c.c. Water = 0.200 gram initially present.

<i>T.</i>	<i>y.</i>	<i>k.c.</i> × 10 ⁴ .		
		<i>r</i> = 0.07	0.09	0.10
[0.0	34.05]	—	—	—
21.0	33.43	—	—	—
30.5	33.27	—	—	—
49.0	32.61	—	—	—
122.0	30.17	—	—	—
294.5	25.74	3.23	3.42	3.52
436.0	22.69	3.32	3.50	3.59
555.0	20.85	3.23	3.40	3.49
681.5	18.79	3.27	3.47	3.56
Mean		3.26	3.45	3.54

As in series II, the value of *r* was 0.09.

SERIES IV.—Temperature 12°.

Concentration of HCl, 0.0234*N*.

Flask I: Volume 50.16 c.c. No water initially present.

<i>T.</i>	<i>y.</i>	<i>k.c.</i> × 10 ⁴ .	
		<i>r</i> = 0.07	0.08
[0.0	34.91]	—	—
30.0	32.13	—	—
51.5	30.39	—	—
125.5	26.09	2.80	3.03
228.5	22.19	2.82	3.00
381.5	18.05	2.89	3.03
562.5	14.81	2.84	2.99
771.5	12.13	2.81	2.94
Mean.....		2.83	2.99

Flask II: Volume 50.18 c.c. Water=0.100 gram initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>	
		<i>r</i> =0.07	0.08
[0.0	34.91]	—	—
34.5	33.44	—	—
54.0	32.58	—	—
148.5	28.86	2.84	2.97
283.5	24.85	2.87	2.99
463.0	20.97	2.86	2.97
625.5	18.22	2.86	2.97
776.5	16.23	2.85	2.94
Mean.....		2.85	2.97

Flask III: Volume 50.18 c.c. Water=0.160 gram initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>	
		<i>r</i> =0.07	0.08
[0.0	34.91]	—	—
24.5	34.15	—	—
60.5	32.67	—	—
197.0	28.77	2.81	2.91
322.5	25.97	2.74	2.84
482.0	22.85	2.77	2.86
652.0	20.32	2.72	2.84
786.5	18.50	2.75	2.84
Mean.....		2.76	2.86

The value of *r* evidently lay between 0.07 and 0.08.

SERIES V.—Temperature 12°.

Concentration of HCl, 0.0234*N*.

Flask I: Volume 50.16 c.c. No water added.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>	
		<i>r</i> =0.07	0.08
[0.0	23.66]	—	—
36.5	21.07	—	—
55.5	19.75	—	—
139.0	16.30	3.02	3.27
254.0	13.10	3.02	3.25
395.0	10.47	3.02	3.21
575.5	8.00	3.03	3.25
695.5	6.83	3.02	3.24
Mean		3.02	3.24

Flask II: Volume 50.18 c.c. 0.100 gram of water added.

<i>T.</i>	<i>y.</i>	<i>k.c.</i> $\times 10^4$.	
		<i>r</i> =0.07	0.08
[0.0	23.66]	—	—
21.0	22.87	—	—
59.5	21.35	—	—
143.5	19.23	2.95	3.08
289.5	16.03	2.97	3.09
459.0	13.41	2.93	3.06
634.0	11.22	2.96	3.07
720.0	10.35	2.96	3.07
Mean.....		2.96	3.07

The value of *r* evidently lies close to 0.07.

SERIES VI.—Temperature 6°.

Concentration of HCl, 0.0303*N*.

Flask I: Volume 50.18 c.c. Water=0.100 gram initially present.

<i>T.</i>	<i>y.</i>	<i>k.c.</i> $\times 10^4$.		
		<i>r</i> =0.04	0.06	0.07
[0.0	34.63]	—	—	—
27.5	33.44	—	—	—
63.0	32.00	—	—	—
258.0	26.06	2.17	2.39	2.50
373.0	23.68	2.14	2.34	2.44
491.0	21.70	2.10	2.29	2.43
621.5	19.70	2.11	2.29	2.38
721.0	18.22	2.16	2.33	2.42
Mean.....		2.14	2.33	2.43

Flask II: Volume 50.15 c.c. Water=0.140 gram initially present.

<i>T.</i>	<i>y.</i>	<i>k.c.</i> $\times 10^4$.		
		<i>r</i> =0.04	0.06	0.07
[0.0	25.43]	—	—	—
17.0	24.91	—	—	—
53.0	23.83	—	—	—
297.5	19.30	2.09	2.27	2.42
430.0	17.21	2.16	2.34	2.43
491.0	16.33	2.19	2.37	2.46
630.5	15.10	2.07	2.23	2.31
721.0	14.38	2.02	2.17	2.25
Mean		2.11	2.28	2.38

Flask III: Volume 50.12 c.c. No water initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>		
		<i>r</i> =0.04	0.06	0.07
[0.0	25.98]	—	—	—
15.0	24.46	—	—	—
52.0	22.27	—	—	—
232.5	15.88	2.01	2.40	2.60
338.0	13.84	2.00	2.35	2.53
490.5	11.36	2.08	2.39	2.56
618.0	9.83	2.06	2.35	2.50
707.0	8.92	2.08	2.37	2.51
Mean		2.05	2.37	2.54

Flask IV: Volume 50.14 c.c. No water initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>		
		<i>r</i> =0.04	0.06	0.07
[0.0	34.26]	—	—	—
27.0	32.12	—	—	—
62.5	29.64	—	—	—
233.0	22.70	1.87	2.21	2.38
340.5	19.93	1.94	2.24	2.39
491.5	17.01	1.99	2.26	2.40
617.5	15.18	1.99	2.24	2.37
711.0	14.00	2.00	2.24	2.36
Mean		1.96	2.24	2.38

The best agreement is given by *r*=0.06.

SERIES VII.—Temperature 6°.

Concentration of HCl, 0.0453*N*.

Flask I: Volume 50.18 c.c. No water initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>	
		<i>r</i> =0.06	0.07
[0.0	24.68]	—	—
18.0	22.71	—	—
39.0	20.60	—	—
178.0	14.61	3.39	3.67
293.0	11.42	3.55	3.87
353.0	10.39	3.50	3.72
440.0	8.88	3.55	3.78
530.0	7.74	3.52	3.74
Mean.....		3.51	3.77

Flask II: Volume 50.14 c.c. 0.100 Gram of water added.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>	
		<i>r</i> =0.06	0.07
[0.0	24.99]	—	—
27.0	23.59	—	—
45.0	22.71	—	—
209.0	17.57	3.51	3.62
300.0	15.22	3.69	3.86
360.0	14.10	3.66	3.81
450.0	12.57	3.66	3.81
537.5	11.38	3.65	3.80
Mean.....		3.63	3.80

The value of *r* is evidently 0.07.

SERIES VIII.—Temperature 0°.

Concentration of HCl, 0.0171*N*.

Flask I: Volume 50.18 c.c. No water initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>	
		<i>r</i> =0.05	0.06
[0.0	33.80]	—	—
50.5	32.41	—	—
86.0	31.42	—	—
154.0	29.60	—	—
361.0	26.20	—	—
839.5	20.96	0.690	0.747
1158.0	18.75	0.682	0.732
1728.0	15.56	0.699	0.745
2277.0	13.45	0.680	0.720
2825.0	11.52	0.693	0.731
Mean		0.689	0.735

Flask II: Volume 50.17 c.c. Water=0.180 gram initially present.

<i>T.</i>	<i>y.</i>	<i>k.c. × 10⁴.</i>	
		<i>r</i> =0.05	0.06
[0.0	35.60]	—	—
62.0	34.98	—	—
130.0	34.63	—	—
167.0	33.79	—	—
870.0	28.74	0.698	0.724
1179.0	26.98	0.689	0.714
1729.0	24.14	0.697	0.719
2288.0	21.90	0.686	0.706
2906.0	19.67	0.687	0.704
Mean		0.691	0.713

The value of *r* was evidently just above 0.05.

SERIES IX.—Temperature 0°.

Concentration of HCl, 0·0171*N*.

Flask I: Volume 50·18 c.c. No water initially present.

<i>T</i> .	<i>y</i> .	<i>k.c.</i> × 10 ⁴ .	
		<i>r</i> =0·05	0·06
[0·0	36·42]	—	—
51·5	35·13	—	—
91·0	34·21	—	—
213·5	30·95	—	—
654·0	25·09	0·649	0·715
1104·0	21·21	0·664	0·716
1473·0	18·81	0·669	0·716
1851·0	16·78	0·680	0·720
2346·0	14·73	0·680	0·721
2943·0	12·67	0·684	0·723
Mean		0·672	0·720

Flask II: Volume 50·17 c.c. Water=0·200 gram initially present.

<i>T</i> .	<i>y</i> .	<i>k.c.</i> × 10 ⁴ .	
		<i>r</i> =0·05	0·06
[0·0	37·67]	—	—
57·5	37·33	—	—
96·5	37·09	—	—
222·5	36·31	—	—
1113·0	29·60	—	—
1485·0	27·67	0·682	0·703
1862·0	25·83	0·686	0·706
2341·0	23·83	0·683	0·703
2941·0	21·78	0·672	0·690
Mean		0·681	0·700

The value of *r* evidently lay nearer 0·05 than 0·06.

SERIES X.—Temperature 0°.

Concentration of HCl, 0·01176*N*.

Flask I: Volume 50·18 c.c. No water initially present.

<i>T</i> .	<i>y</i> .	<i>k.c.</i> × 10 ⁴ .	
		<i>r</i> =0·05	0·06
[0·0	27·20]	—	—
65·5	26·08	—	—
130·5	24·96	—	—
532·0	20·32	0·489	0·542
1162·0	16·33	0·486	0·527
1889·0	13·11	0·503	0·541
2940·0	10·12	0·505	0·526
4068·0	7·87	0·509	0·538
Mean.....		0·501	0·535

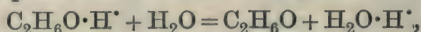
Flask II: Volume 50.16 c.c. Water=0.160 gram initially present.

T.	y.	$k.c. \times 10^4.$	
		$r=0.05$	0.06
[0.0	28.35]	—	—
80.5	27.91	—	—
141.0	27.58	—	—
1183.0	22.55	0.501	0.520
1903.0	20.01	0.500	0.517
2961.0	17.14	0.491	0.508
4063.0	14.94	0.476	0.492
Mean.....		0.492	0.509

The value of r evidently lay near 0.05.

Adopting the hypothesis that the changes in the value of r are due to changes in the basic affinity of the solvent, then the applicability of the formula $P = \frac{P_0 r}{r + w}$ (Trans., 1910, 97, 22) shows that, if the molecule of water in moist alcohol has the formula $(H_2O)_x$, the hydrated hydrions in that solvent may be represented as $(H_2O)_x \cdot H^+$.

If K' is the equilibrium constant for the reaction



then $K' = \frac{\text{a constant}}{r}$ and $d(\log_e k) = -d(\log_e r)$, so that if the heat of the reaction is q , then $\frac{d(\log_e r)}{dT} = \frac{q}{RT^2}$, and if q is nearly constant (as doubtless it is for the small temperature range 0° to 25°):

$$\log_e r - \log_e r' = \frac{q}{R} \left(\frac{1}{T'} - \frac{1}{T} \right)$$

where r and r' are the water values at the absolute temperatures T and T' respectively. On the assumption that 0.097 and 0.050 are the probable values at 25° and 0° respectively, the preceding equation takes the form:

$$\log_{10} r = 2.130 - \frac{936.7}{T},$$

the corresponding value for q being, roughly, 4300 gram-calories. In the following table, under r (calc.) are given values of r calculated from this equation.

These values are compared in the table with the corresponding values r_t measured by the tintometric method, and with r_E measured by the esterification method, during the present investigation.

T (degrees centigrade).	r (calc.) $\times 10^3$.	$r_i \times 10^3$.	$r_E \times 10^3$.
25	[97]	94, 98, 98	95
22	90	90	—
19	83	86	—
18	81	86	90, 90
17	79	76, 80	—
15	75	73, 80	—
12	70	68, 70, 80	70, 75
10	66	66, 68	—
8	62	63	—
6	59	—	60, 70
5	58	58	—
2	53	50, 52	—
1	51	55	—
0	[50]	—	50, 52, 50

The relative experimental error is evidently still very considerable. This is probably due mainly to the great sensitiveness of the solutions to traces of basic impurities, and the values of r_E are, on the whole, certainly somewhat higher than the corresponding values of r_i ; the latter circumstance is probably the result of the greater degree of ionisation of the hydrogen chloride.

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THE CHEMICAL LABORATORIES,
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XCVIII.—*The Constituents of Bryony Root.*

By FREDERICK BELDING POWER and CHARLES WATSON MOORE.

BRYONY root has been used medicinally from a very remote period on account of its cathartic properties, and was formerly recognised by several of the national Pharmacopoeias, but is now rarely employed. The plants yielding this root are *Bryonia alba*, Linné, and *Bryonia dioica*, Linné (Nat. Ord., *Cucurbitaceae*), which are botanically closely allied. They are indigenous to the greater part of Europe, but the last-named species is the only one of the genus commonly found in this country, and, therefore, is frequently designated as English bryony. The roots of the two species are generally considered to possess the same properties, and they appear to be indiscriminately collected, although it has been asserted by Petresco (*United States Dispensatory*, 18th edition, p. 279) that they differ appreciably in their physiological action.

Bryony root has been the subject of several investigations, chiefly for the purpose of determining the nature of its active constituent (compare Husemann, *Die Pflanzenstoffe*, second edition, p. 1349, and van Ryn, *Die Glykoside*, p. 463), but no complete chemical examination has hitherto been made of it. With the exception of the recorded presence of starch, gum, sugar, and fat, the information concerning the constituents of the root is, in fact, chiefly restricted to the statement that it contains an amorphous, bitter glucoside, designated as bryonin. This product, as obtained by Masson (*J. Pharm. Chim.*, 1893, [v], **27**, 300), formed pale yellow, amorphous laminæ or a white, amorphous powder, soluble in water and in alcohol, but insoluble in ether, and possessing a strongly bitter taste. It was stated to have the formula $C_{34}H_{48}O_9$, and, on heating with dilute sulphuric acid, to yield dextrose and an amorphous, yellow resin, designated as bryogenin, $C_{28}H_{38}O_4$. Another product obtained by Masson (*loc. cit.*), which was of a purely resinous nature, was termed bryoresin, and to this the formula $C_{37}H_{68}O_{18}$ was assigned.

A consideration of the method of preparation and characters of the so-called bryonin, as described in the literature, renders it apparent that it could not have represented a pure or homogeneous substance. Inasmuch as the present authors have recently made a complete examination of two other drugs obtained from cucurbitaceous plants, namely, elaterium (*Pharm. J.*, 1909, **83**, 501; *Trans.*, 1909, **95**, 1985) and colocynth (*Trans.*, 1910, **97**, 99), it was deemed of interest also to investigate the constituents of bryony root, especially as the latter is known to possess active purgative properties. The results of the present chemical investigation, and of the physiological tests, are summarised at the end of this paper.

EXPERIMENTAL.

The material employed for this investigation consisted of the roots of *Bryonia dioica*, Linné, which had been specially collected for us during the early part of October by Messrs. W. Ransom and Son, of Hitchin, under the personal superintendence of Mr. P. E. F. Perrédès, B.Sc., F.L.S. Our thanks are due to these gentlemen for the great care which they have exercised in this connexion.

The amount of fresh root collected was 107.5 kilograms, and this, after being sliced and dried, weighed 25.5 kilograms. The loss on drying was therefore equivalent to 76.3 per cent. of the original weight.

Separation of an Enzyme.

With consideration of the previously recorded statements (*loc. cit.*) that bryony root contains a glucoside, it was thought desirable to examine it for the presence of an enzyme. For this purpose one kilogram of the finely ground material was mixed with sufficient water to cover it, and the mixture kept for several hours, after which the aqueous liquid was expressed and filtered. To this liquid, in which the presence of starch was indicated, about twice its volume of alcohol was added, when a voluminous, light brown precipitate was produced. This was collected, washed with a little alcohol, and dried in a vacuum over sulphuric acid. It then amounted to 35 grams, or 3·5 per cent. of the weight of dried root employed. This product yielded the biuret reaction, and slowly hydrolysed both amygdalin and salicin, as also the glucosidic constituent of bryony root, which will subsequently be described.

Test for an Alkaloid.—Ten grams of the finely ground root were digested with Prollius' fluid, and the resulting liquid subjected to the usual tests for an alkaloid. The reactions thus obtained indicated the presence of a relatively small amount of such a substance.

Preliminary Extraction of the Root.—Twenty-five grams of the ground material were extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°) extracted	0·19 gram	=	0·76 per cent.
Ether	0·22 "	=	0·88 " "
Chloroform	0·52 "	=	2·08 " "
Ethyl acetate	0·80 "	=	3·20 " "
Alcohol	2·70 "	=	10·80 " "

Total 4·43 grams = 17·72 per cent.

For the purpose of a complete examination, 23·9 kilograms of the ground bryony root were completely extracted with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 6·3 kilograms.

Distillation of the Extract with Steam. Separation of an Essential Oil.

A quantity (2 kilograms) of the above-mentioned extract, representing 7·6 kilograms of the ground root, was mixed with water, and steam passed through the mixture for some hours. The distillate, which amounted to 2·5 litres, contained some drops of oil floating on the surface. It was extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a small

quantity of an essential oil was obtained. This was a pale yellow liquid, which possessed a characteristic odour. The amount of this oil was, however, too small to permit of its further investigation.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam, as above described, there remained in the distillation flask a dark-coloured, aqueous liquid (A) and a quantity of a brown resin (B). The latter was collected, and repeatedly washed with water until nothing further was removed, the washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

Isolation of a Crystalline, Neutral Substance, $C_{20}H_{30}O_5$.

The aqueous liquid (A), which amounted to 5 litres, was repeatedly extracted with ether, the ethereal extracts being then united, washed with water, and concentrated to the volume of 500 c.c. The ethereal solution so obtained was extracted successively with dilute hydrochloric acid, aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide, which, however, only removed small quantities of resinous products. The ethereal solution was accordingly washed with water, dried, and the solvent evaporated, when a quantity of a syrupy liquid remained, from which a crystalline substance slowly separated. The mixture was diluted with ether, and the crystalline material collected. It formed small, colourless needles, melting at about 220° , and amounted to 1.5 grams. After recrystallisation from alcohol, and then again from ether, it separated in glistening needles, melting and decomposing at $220-222^{\circ}$:

0.1358 gave 0.3407 CO_2 and 0.1090 H_2O . $C=68.4$; $H=8.9$.

After another crystallisation from ether it was again analysed:

0.1352 gave 0.3390 CO_2 and 0.1090 H_2O . $C=68.4$; $H=8.9$.

$C_{20}H_{30}O_5$ requires $C=68.6$; $H=8.6$ per cent.

The molecular weight of the substance was determined by the cryoscopic method:

0.3688, in 22.93 of acetic acid, gave $\Delta t = 0.199^{\circ}$. M.W. = 315.

$C_{20}H_{30}O_5$ requires M.W. = 350.

$C_{16}H_{24}O_4$ „ M.W. = 280.

The substance thus appears to possess the formula $C_{20}H_{30}O_5$, although the formula $C_{16}H_{24}O_4$ is not excluded, and it is evidently a new compound.

A determination of its specific rotatory power gave the following result:

0.3040, made up to 20 c.c. with chloroform, gave $\alpha_D + 1^{\circ}47'$ in a 2-dcm. tube, whence $[\alpha]_D + 58.6^{\circ}$.

The substance is moderately soluble in alcohol, but very sparingly so in ether, and practically insoluble in water. It contains no methoxyl group, and no crystalline acetyl or other derivative could be prepared from it.

Isolation of an Amorphous, Glucosidic Product.

The original aqueous liquid (A) which had been extracted by means of ether, as above described, was thoroughly extracted with successive portions of amyl alcohol. These extracts were united, washed with water, and concentrated to a volume of 1.5 litres, when, on cooling, a considerable quantity (70 grams) of a light brown, amorphous product separated. This was collected, washed first with a little dry amyl alcohol, then with ethyl acetate, and subsequently extracted with the latter solvent in a Soxhlet apparatus. A relatively small portion of the product was thus removed, and formed, when dry, a yellowish-brown, amorphous powder. This was readily soluble in alcohol and in water, but all attempts to obtain it in a crystalline condition were unsuccessful. It possessed a bitter taste, and its aqueous solution gave a dense precipitate with tannic acid, but no coloration with ferric chloride. When heated with dilute sulphuric acid it was rapidly hydrolysed, with the production of a brown resin and a sugar, which yielded *d*-phenyl-glucosazone, melting at 208—210°. Its hydrolysis was also slowly effected by the enzyme contained in the root, although emulsin appeared to have little or no action on it. In view of the glucosidic character of the product, a portion of it was heated with acetic anhydride in the presence of a little *d*-camphorsulphonic acid. A vigorous reaction ensued, but no crystalline acetyl derivative could be obtained.

Isolation of an Amorphous Alkaloidal Principle.

The amyl-alcoholic mother liquors remaining from the separation of the above-described glucosidic product were diluted with amyl alcohol, and repeatedly shaken with dilute hydrochloric acid. The acid extracts were united, made alkaline with ammonia, and extracted with amyl alcohol, when a small quantity of material was removed, which was weakly basic, and responded to the usual alkaloid reagents. This product formed a brownish-yellow, intensely bitter, amorphous powder, which was soluble in water and in

alcohol, but almost insoluble in ether or chloroform. Its aqueous solution gives an abundant precipitate with tannic acid. When heated with hydrochloric acid, it was rapidly decomposed, with the formation of ammonia, and the latter was also evolved on heating the substance with alkali hydroxides. The alkaloidal principle appears to be incapable of forming any crystalline salt.

The original aqueous liquid, after being extracted with amyl alcohol as above described, was treated with a slight excess of a solution of basic lead acetate. A copious brown precipitate was thus produced, which, however, when decomposed by hydrogen sulphide, yielded nothing definite. The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the lead, and the filtered liquid concentrated to the consistency of a thin syrup. This contained a considerable quantity of sugar, since it readily yielded *d*-phenylglucosazone, melting at 208—210°.

Examination of the Resin (B).

The resin was a dark brown, viscid product, and amounted to 160 grams, being thus equivalent to about 2 per cent. of the weight of dried root employed. It was dissolved in alcohol, mixed with purified sawdust, and the dried mixture extracted successively in a Soxhlet apparatus with light petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

Isolation of a Phytosterol, C₂₇H₄₆O.

The petroleum extract was a viscid liquid, and amounted to 99 grams. It was dissolved in ether, and the ethereal solution shaken with aqueous potassium carbonate, which, however, only removed traces of fatty acids. The ether was accordingly evaporated, and the residue hydrolysed by boiling for some time with an alcoholic solution of potassium hydroxide. The alcohol was then evaporated, water added, and the alkaline aqueous liquid extracted with ether, the ethereal liquid being dried and the solvent removed, when a crystalline residue was obtained. This was recrystallised from a mixture of dilute alcohol and ethyl acetate, when it formed glistening plates, melting at 137°. The amount of this substance was 2·5 grams:

0·7532, on heating at 110°, lost 0·0354 H₂O. H₂O=4·7.

0·1468 * gave 0·4490 CO₂ and 0·1590 H₂O. C=83·4; H=12·0.

C₂₇H₄₆O, H₂O requires H₂O=4·5 per cent.

C₂₇H₄₆O requires C=83·9; H=11·9 per cent.

* Anhydrous substance.

The substance thus agrees in composition with a phytosterol, and it yielded the colour reactions of that class of compounds. It was found to be optically inactive, as was also the case with the phytosterol obtained by the present authors from colocynth, although the two compounds are not identical (compare *Trans.*, 1910, **98**, 105). The acetyl derivative, when crystallised from acetic anhydride, separated in glistening plates, melting at 155—157°.

Isolation of a New Dihydric Alcohol, Bryonol, $C_{22}H_{34}O_2(OH)_2$.

The alkaline liquid, which had been extracted with ether as above described, was acidified, and again extracted with ether. The ethereal extracts were united, after which a quantity of an almost colourless, sparingly soluble substance which accompanied them was separated by filtration. This substance was crystallised, first from a mixture of pyridine and ethyl acetate, and then from glacial acetic acid, when it was obtained in small, colourless plates, melting and decomposing at 210—212°. The quantity so obtained was about 0.8 gram:

0.1324 gave 0.3508 CO_2 and 0.1210 H_2O . $C=72.3$; $H=10.1$.

$C_{22}H_{36}O_4$ requires $C=72.4$; $H=9.9$ per cent.

This substance, when dissolved in chloroform with a little acetic anhydride, gave, on the addition of a few drops of concentrated sulphuric acid, a series of colour reactions similar to those produced by the dihydric alcohol ipurganol, $C_{21}H_{32}O_2(OH)_2$ (Power and Rogerson, *J. Amer. Chem. Soc.*, 1910, **32**, 89), and it appears, in fact, to be the next higher homologue of the latter. Like ipurganol, it dissolves in concentrated sulphuric acid with a yellow colour, the solution showing a green fluorescence.

No substance possessing the formula of that above described appears to have hitherto been recorded. Being, therefore, a new compound, it is proposed to designate it *bryonol*, with reference to the generic name of the plant from which it has been isolated.

Diacetylbryonol, $C_{22}H_{34}O_4(CO \cdot CH_3)_2$.—This was obtained by heating bryonol with acetic anhydride. It crystallises from alcohol in long needles, melting at 152°:

0.1184 gave 0.3000 CO_2 and 0.0960 H_2O . $C=69.1$; $H=9.0$.

$C_{26}H_{40}O_6$ requires $C=69.6$; $H=8.9$ per cent.

From the above results it is evident that bryonol belongs to a group of dihydric alcohols which are represented by the general formula $C_nH_{2n-8}O_4$. The known members of this group, all of which have been isolated in these laboratories, now comprise the following compounds: ipurganol, $C_{21}H_{32}O_2(OH)_2$ (*loc. cit.*); *bryonol*,

$C_{22}H_{34}O_2(OH)_2$; grindelol, $C_{23}H_{36}O_2(OH)_2$ (*Proc. Amer. Pharm. Assoc.*, 1907, **55**, 342); and cucurbitol, $C_{24}H_{38}O_2(OH)_2$ (*J. Amer. Chem. Soc.*, 1910, **32**, 367).

Examination of the Fatty Acids.

The ethereal liquid, from which the bryonol had been separated by filtration, as above described, was washed, dried, and the solvent removed, when a quantity (20 grams) of fatty acids was obtained, which, when distilled under diminished pressure, passed over between 230° and $260^\circ/15$ mm. The mixed acids were converted into their lead salts, and the latter digested with ether, when a portion dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of lead salts yielded 11 grams of liquid acids, whilst the insoluble portion gave 8.5 grams of solid acids.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 220° and $230^\circ/15$ mm. An analysis and a determination of the iodine value gave the following results:

0.1373 gave 0.3865 CO_2 and 0.1390 H_2O . C=76.8; H=11.2.

0.3195 absorbed 0.5410 iodine. Iodine value=170.

$C_{18}H_{34}O_2$ requires C=76.6; H=12.1 per cent. Iodine value=90.1.

$C_{18}H_{32}O_2$ „ C=77.1; H=11.4 „ „ Iodine value=181.4.

It thus appears that the liquid acids consisted of a mixture of oleic and linolic acids, the latter predominating.

The Solid Acids.—These acids melted at $55-57^\circ$, and on analysis gave the following result:

0.1436 gave 0.3982 CO_2 and 0.1620 H_2O . C=75.6; H=12.6.

$C_{16}H_{32}O_2$ requires C=75.0; H=12.1 per cent.

$C_{18}H_{36}O_2$ „ C=76.1; H=12.7 „ „

From this result it is evident that the solid acids consisted of a mixture of palmitic and stearic acids, and apparently in about equal proportions.

Ether, Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

These extracts amounted to 25, 15, 2, and 15 grams respectively. They were dark-coloured resins, and, with the exception of about 0.2 gram of the previously-described crystalline, neutral substance, which was isolated from the ethereal extract, nothing definite could be isolated from them.

Summary.

The material employed for the present investigation consisted of the roots of *Bryonia dioica*, Linné, which had been specially collected for the purpose.

The roots were found to contain an enzyme, which was obtained in the form of a light brown powder. This product slowly hydrolysed the glucosidic constituent of the root, and also effected the hydrolysis of amygdalin and salicin.

An alcoholic extract of the dried roots, when distilled in a current of steam, yielded a small amount of a pale yellow essential oil, which possessed a characteristic odour. From the portion of the extract which was soluble in water there were isolated: (i) a small amount of a colourless, crystalline, neutral substance (m. p. 220—222°), which appears to possess the formula $C_{20}H_{30}O_5$, and has $[\alpha]_D + 58.6^\circ$; (ii) an amorphous, glucosidic product, having a brown colour and a bitter taste, which, when hydrolysed by heating with dilute sulphuric acid or by the enzyme contained in the root, yielded a brown resin and a sugar, from which *d*-phenylglucosazone (m. p. 208—210°) was prepared; (iii) an amorphous, alkaloidal principle, possessing a brownish-yellow colour and an intensely bitter taste, but which was very weakly basic, and appeared to be incapable of forming any crystalline salt. The aqueous liquid contained, furthermore, a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 208—210°).

The portion of extract which was insoluble in water consisted of a dark brown, viscid resin, amounting to about 2 per cent. of the weight of dried root employed. From this material the following compounds were isolated: (i) a phytosterol, $C_{27}H_{46}O$ (m. p. 137°), which was optically inactive; (ii) a new dihydric alcohol, *bryonol*, $C_{22}H_{34}O_2(OH)_2$, melting at 210—212°, and yielding a *diacetyl* derivative, melting at 152°. *Bryonol* evidently belongs to a group of dihydric alcohols possessing the general formula $C_nH_{2n-8}O_4$, which comprises the following additional compounds: *ipurganol*, $C_{21}H_{32}O_2(OH)_2$, *grindelol*, $C_{23}H_{36}O_2(OH)_2$, and *cucurbitol*, $C_{24}H_{38}O_2(OH)_2$; (iii) a mixture of fatty acids, consisting of oleic, linolic, palmitic, and stearic acids.

Inasmuch as both the above-mentioned glucosidic product and the alkaloidal principle, as well as the aqueous liquid from which they had been removed, were abundantly precipitated by tannic acid, it follows that the preparations obtained by previous investigators by means of this reagent, which were regarded as a glucoside and designated "*bryonin*," must have consisted of complex mixtures, the constituents of which, moreover, were not entirely glucosidic.

The various chemical formulæ that have been assigned to these amorphous compounds are accordingly in the highest degree fallacious.

In order to ascertain the source of activity of the root, a number of products obtained in the course of the present investigation were kindly tested for us by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, to whom our best thanks may here be expressed. All the experiments were conducted with small dogs.

The crystalline, neutral substance, $C_{20}H_{30}O_5$, and the glucosidic product, in amounts of 0.1 gram, had no effect. The alkaloidal principle, in the same dose, produced slight purgation. The portion of the alcoholic extract which was soluble in water, and from which the above-mentioned products had previously been removed by successive extraction with ether and amyl alcohol, had no appreciable effect in amounts corresponding to about 4 grams of the dried root. The resinous material of the root, as well as the products obtained by its successive extraction with light petroleum, ether, chloroform, and ethyl acetate, produced marked purgation in doses of 1 gram, whereas the final alcohol extract of the resin had practically no effect.

From the above results it is obvious that the activity of bryony root cannot be attributed to a single definite principle, and it would appear that its purgative property resides chiefly in the resinous and alkaloidal constituents. The assumption of previous investigators that the active principle is a glucoside, has thus been shown to be incorrect.

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XCIX.—*The Constituents of Rhubarb.*

By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

PERHAPS no drug recognised by any of the national Pharmacopœias has more frequently engaged the attention of chemists than rhubarb. Notwithstanding this fact, it appeared to the present authors that our knowledge respecting the constituents of this drug was by no means complete, and a thorough investigation of the subject was therefore undertaken.

Amongst the earliest communications on the subject were those by Geiger (*Annalen*, 1823, **8**, 47; 1824, **9**, 91, 304), who described

a product called "rhabarberin." This was shown by Schlossberger and Döpping (*Annalen*, 1844, **50**, 214) to be identical with chrysophanic acid, which had, in the meantime, been described by Rochleder and Heldt, but it would appear probable that it was a mixture of this compound and emodin monomethyl ether. De la Rue and Müller (*Journ. Chem. Soc.*, 1857, **10**, 298) examined a deposit from "*Extractum Rhei*," from which they obtained "chrysophane" and a new compound, designated as emodin. Hesse (*Pharm. J.*, 1895, [iv], I, 352; and *Annalen*, 1899, **309**, 32) recorded the occurrence in rhubarb of rhein and "rhabarberon" (an isomeride of emodin), but was unable to isolate pure chrysophanic acid, this being always associated with a methylated constituent, which was assumed to be a methyl ether of chrysophanic acid. The next communication of importance on Chinese rhubarb was by Tschirch and Heuberger (*Arch. Pharm.*, 1902, **204**, 596), who failed to obtain the "rhabarberon" of Hesse, but isolated gallic acid, a substance giving the reactions of a cholesterol, impure chrysophanic acid, emodin, rhein, and two amorphous, glucosidic products, namely, rheotannoglucoside and rheoanthraglucoside. The former of these products, on hydrolysis, gave a lævorotatory sugar and small amounts of gallic and cinnamic acids, together with amorphous products, whilst the latter "glucoside" yielded a dextrorotatory sugar, small amounts of the acids mentioned, a mixture of anthraquinone derivatives, and amorphous material. Eyken (*Pharm. Weekblad*, 1904, **41**, 177) isolated impure chrysophanic acid, emodin, "isoemodin," and rhein, together with "anthraglucosides," and Tschirch and Eyken (*Schweiz. Woch. Pharm.*, 1904, Nos. 40 and 41) stated that "isoemodin" is probably identical with Hesse's "rhabarberon." Gilson (*Compt. rend.*, 1903, **136**, 385) claimed to have isolated two crystalline glucosides, "glucogalline" and "tétrarine." The former of these was stated to yield dextrose and gallic acid, whilst the latter gave the same sugar, gallic and cinnamic acids, and "rhéosmine." Quite recently, Oesterle and Johann (*Arch. Pharm.*, 1910, **248**, 476) showed in an indirect way that the methylated substance with which the chrysophanic acid from rhubarb is invariably associated was emodin monomethyl ether, identical with that associated with chrysophanic acid in *Rumex Ecklonianus*, Meissner (Tutin and Clewer, *Trans.*, 1910, **97**, 1).

In addition to the compounds mentioned in the foregoing review of the literature, most of the above-mentioned investigators also describe, under various names, a number of amorphous products, which were obviously of indefinite composition. Mention is several times made, however, of the presence in rhubarb of "glucose" and of a neutral fat.

The results of the present investigation are summarised at the end of this paper, but a few of them may be discussed here.

The present authors have isolated emodin monomethyl ether from rhubarb, thus confirming Oesterle and Johann's statement, and have found that the "rhabarberon" of Hesse and the "isoemodin" of Tschirch and Eyken were really only somewhat impure aloemodin. A new anthraquinone derivative, $C_{17}H_{10}O_6$, which it is proposed to designate *rheinolic acid*, has also been isolated. The opinion of Tschirch and Heuberger (*loc. cit.*) that rhubarb contains two glucosides, "rheotannoglucoside" and "rheoanthraglucoside," cannot be accepted. A mixture of the glucosides of rhein, emodin, aloemodin, emodin monomethyl ether, and chrysophanic acid occurs in rhubarb, and when free from resin this mixture crystallises well, but it is entirely devoid of purgative action. The mother liquors from the anthraquinone glucosides yielded, however, a quantity of a non-glucosidic resin, which was strongly purgative. The "rheoanthraglucoside" of Tschirch and Heuberger, which was amorphous, was evidently a mixture of the non-glucosidic resin and the glucosides of the anthraquinone derivatives. Only a relatively small amount of a product which can properly be called a tannin is present in rhubarb, free gallic acid, which is present in very large amount, being the chief astringent constituent of the drug. No glucoside of gallic acid is present, but this acid, together with cinnamic acid, occurs to a small extent as an ester, although the latter acid, like the former, is chiefly present in the free state. The sugar yielded by the various glucosidic products was in every case dextrose. It is evident, therefore, that the levorotatory sugar obtained by Tschirch and Heuberger from their "rheotannoglucoside" must have contained considerable levulose, which had been occluded in the indefinite mixture which was regarded by them as a glucoside.

The only anthraquinone derivatives present in rhubarb which possess a purgative action are aloemodin and chrysophanic acid, but neither of these is nearly so active as the resin.

Finally, it may be of interest to recall the present state of our knowledge regarding the mutual relationship of the anthraquinone derivatives occurring in rhubarb: Chrysophanic acid* is a dihydroxymethylanthraquinone, but the relative positions of the groups is not known with certainty. Emodin is a hydroxychrysophanic acid, whilst emodin monomethyl ether is the corresponding methoxychrysophanic acid. Aloe-emodin is the primary alcohol

* The name "chrysophanic acid" is misleading, as the substance contains no carboxyl group. Chrysophanol would be a much more appropriate designation for the compound in question (compare *Arch. Pharm.*, 1911, 249, 222).

(hydroxymethyldihydroxyanthraquinone) corresponding with chrysophanic acid, whilst rhein is the corresponding carboxylic acid, and may be formed by the oxidation of aloe-emodin.

EXPERIMENTAL.

The material employed in the present investigation consisted of the best quality of sun-dried "Shensi" rhubarb. As a preliminary experiment, 20 grams of the ground rhizome were extracted successively in a Soxhlet apparatus with various solvents, the following amounts of extract, dried at 110° , being obtained:

Petroleum (b. p. $35-50^{\circ}$) extracted	0.35 per cent.
Ether	4.25 " "
Chloroform	0.85 " "
Ethyl acetate	16.95 " "
Alcohol	21.85 " "
<hr/>	
Total	= 44.25 per cent.

A quantity (20.84 kilograms) of the ground rhizome was then completely extracted by continuous percolation with hot alcohol, and the resulting extract concentrated under diminished pressure, when 10.8 kilograms of a viscid extract containing small lumps of granular solid were obtained. Five kilograms of this extract were then mixed with water, and steam passed through the mixture until volatile products ceased to be removed.

Examination of the Steam Distillate.

The yellow distillate was extracted with ether, and the ethereal liquid shaken successively with aqueous ammonium carbonate,* sodium carbonate, and potassium hydroxide. The ammonium carbonate extract yielded, on acidification, 0.2 gram of a liquid acid, which was identified by the analysis of its silver salt as a hexoic acid.

The sodium carbonate extract yielded a little palmitic acid (m. p. 62°), and the potassium hydroxide extract gave a small amount of a product crystallising in golden-coloured plates, melting at 190° , which was found to be pure chrysophanic acid.

The ethereal liquid which had been extracted with alkalis yielded about 0.5 gram of an essential oil, which possessed in a high degree the characteristic odour of the drug.

* The ammonium carbonate solution referred to throughout this work was prepared by dissolving Kahlbaum's "ammonium carbonate" in water, and then saturating the solution with carbon dioxide.

Non-volatile Constituents of the Extract.

After the steam distillation, the mixture remaining in the flask consisted of a viscid, resinous product, and a dark-coloured, aqueous liquid. The mixture was diluted and allowed to cool, when the resin was separated. The latter was then thoroughly washed several times with hot water, the concentrated washings being added to the original aqueous liquid. There were thus obtained a clear, dark-coloured, aqueous liquid (A), amounting to about 40 litres, and a dark greenish-yellow resin (B), which weighed 414 grams.

Examination of the Aqueous Liquid (A).

The aqueous liquid (A) deposited a brown resinous product on keeping, but this dissolved when the mixture was shaken with ether. The entire aqueous liquid was thoroughly extracted ten times with a large volume of ether, the ethereal liquid being washed and concentrated. To this concentrated liquid was added the ether-soluble portion of the amyl-alcoholic extract, obtained as subsequently described. The concentrated ethereal solution of the entire ether-soluble constituents of the aqueous liquid deposited on keeping a quantity of a semi-crystalline, yellow powder, which was collected. The filtrate was evaporated, and the residue heated with ethyl acetate, when a quantity of a yellow powder remained undissolved. A considerable volume of petroleum (b. p. 35—50°) was then added to the filtered ethyl acetate solution, after which the liquid was decanted from the precipitated tarry product, and evaporated to a small bulk. This treatment with petroleum was twice repeated in a similar manner, when further small precipitates of the yellow powder were obtained, which were added to the similar products mentioned above.

Isolation of Cinnamic Acid.

The product which remained on evaporating the final petroleum solution obtained as above described, was dissolved in ether, and extracted successively with 10 per cent. aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide.

The ammonium carbonate extract, after acidification, deposited 0.5 gram of cinnamic acid (m. p. 131—132°), (Found, C=72.9; H=5.6. Calc., C=73.0; H=5.4 per cent.), a compound which has not previously been recorded as occurring in rhubarb in the free state. The original acid, aqueous filtrates from the cinnamic acid yielded nothing but a further small quantity of the same compound.

The sodium carbonate and potassium hydroxide extracts of the petroleum soluble products yielded only small quantities of alo-

emodin (m. p. 216°) and chrysophanic acid (m. p. 189°) respectively, the isolation of which in larger amount will subsequently be described.

The material remaining dissolved in the ether after extraction with potassium hydroxide consisted of a small amount of fatty matter, which was added to the petroleum extract of the resin (B), subsequently to be described.

Isolation of Rhein, $C_{14}H_5O_2(OH)_2 \cdot CO_2H$.

The several fractions of yellow powder obtained from the ethereal extract of the aqueous liquid were united, and heated with amyl alcohol, the mixture cooled, and then filtered. The material undissolved by this treatment (3 grams) was crystallised three times from pyridine, when glistening, orange-coloured needles were obtained. These crystals fell to a powder when heated at 130° , after which they melted at 318° :

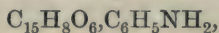
0.1962,* on heating at 130° , lost 0.0421 of pyridine. $C_5H_5N = 21.5$.

0.0889 † gave 0.2055 CO_2 and 0.0230 H_2O . $C = 63.0$; $H = 2.9$.

$C_{15}H_8O_6, C_5H_5N$ requires $C_5H_5N = 21.8$ per cent.

$C_{15}H_8O_6$ requires $C = 63.4$; $H = 2.8$ per cent.

The substance was, therefore, rhein (a dihydroxyanthraquinone carboxylic acid), which is thus seen to separate from pyridine in combination with the latter. It appears to be owing to this salt-formation that rhein, which is nearly insoluble in most solvents, dissolves readily in organic bases; the *aniline* salt,



crystallised in orange-red needles.

Diacetylrhein, $C_{14}H_5O_4Ac_2 \cdot CO_2H$.—The statements in the literature regarding acetylrhein are rather discrepant. Thus, Hesse (*Annalen*, 1899, **309**, 32) stated that rhein yielded a monoacetyl derivative (m. p. $262-263^{\circ}$) and a diacetyl derivative (m. p. 236°). Subsequently Tschirch and Heuberger (*loc. cit.*) obtained only the diacetyl compound, melting at 236° , whilst Oesterle (*Schweiz. Woch. Pharm.*, 1903, **40**, 600) states that this compound melts at $247-248^{\circ}$. Later, Robinson and Simonsen (*Trans.*, 1909, **95**, 1090) prepared diacetylrhein, agreeing in its general properties with this compound as described by Hesse, by Tschirch and Heuberger, and by Oesterle, but they stated that they were able to obtain only anomalous results by its analysis. The present authors, however, have found that pure diacetylrhein, melting at 258° , may readily be obtained by heating rhein for one hour with a large excess of acetic anhydride to which a little camphorsulphonic acid (or

* Air-dried substance.

† Dried at 130° .

pyridine) had been added. After concentration, diacetylrhein separated in rosettes of pale yellow needles, melting at 258° :

0.1152 gave 0.2601 CO_2 and 0.0364 H_2O . $\text{C}=61.6$; $\text{H}=3.5$.

$\text{C}_{19}\text{H}_{12}\text{O}_8$ requires $\text{C}=62.0$; $\text{H}=3.3$ per cent.

Diacetylrhein is readily removed from its solution in immiscible solvents by means of aqueous sodium carbonate, on account of its containing a carboxyl group. The diacetylrhein prepared by the present authors, however, exhibited a remarkable behaviour on heating with xylene. When subjected to this treatment it first entirely dissolved, but then suddenly separated completely from the boiling liquid. The reprecipitated compound was now practically insoluble in all solvents except alkalis, but melted at the same temperature as the original preparation (258°), and, on analysis, appeared to possess the same composition. (Found, $\text{C}=62.1$; $\text{H}=3.4$ per cent.).

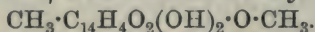
Dibenzoylrhein, $\text{C}_{14}\text{H}_5\text{O}_4\text{Bz}_2\cdot\text{CO}_2\text{H}$.—No benzoyl derivative of rhein has heretofore been described. Rhein was therefore benzoylated by the Schotten-Baumann method, when the *potassium* salt of *dibenzoylrhein* was obtained as a sparingly soluble compound. This was dissolved in glacial acetic acid, when, on cooling, *dibenzoylrhein* separated. After recrystallisation, this compound formed yellowish-brown prisms, melting at 262° :

0.0936 gave 0.2415 CO_2 and 0.0284 H_2O . $\text{C}=70.4$; $\text{H}=3.4$.

$\text{C}_{29}\text{H}_{16}\text{O}_8$ requires $\text{C}=70.7$; $\text{H}=3.3$ per cent.

Dibenzoylrhein is removed from its solution in chloroform by aqueous alkalis.

Isolation of Emodin Monomethyl Ether,



The pyridine mother liquors from which the rhein had been separated, as above described, were evaporated, and the residue was dissolved in the original amyl alcohol solution from which the crude rhein had been separated. The solution was then concentrated somewhat, when, on cooling, about 2 grams of emodin monomethyl ether (m. p. 195° . Found, $\text{C}=67.3$; $\text{H}=4.3$. Calc., $\text{C}=67.6$; $\text{H}=4.2$ per cent.) were obtained. It was found to be identical with the product obtained by the present authors from *Rumex Ecklonianus*, Meissner (*loc. cit.*), and the synthetical ether prepared from emodin by Jowett and Potter (Trans., 1903, **77**, 1330). Its identity was further confirmed by the formation of its diacetyl derivative, which melted at 186° , and by its conversion into emodin by means of concentrated sulphuric acid.

Emodin monomethyl ether has not previously been obtained from

rhubarb, but, after it had been thus isolated by the present authors, it was shown by Oesterle and Johann (*loc. cit.*) to be the methylated compound which is associated with chrysophanic acid in this drug.

Dibenzoylmodin Monomethyl Ether, $\text{CH}_3 \cdot \text{C}_{14}\text{H}_4\text{O}_4\text{Bz}_2 \cdot \text{O} \cdot \text{CH}_3$, was prepared by the Schotten-Baumann reaction. It crystallised readily from a mixture of glacial acetic acid and alcohol in long, silky, pale yellow needles, melting at 228° :

0.1000 gave 0.2680 CO_2 and 0.0366 H_2O . $\text{C}=73.1$; $\text{H}=4.1$.

$\text{C}_{30}\text{H}_{20}\text{O}_7$ requires $\text{C}=73.2$; $\text{H}=4.1$ per cent.

It was known that the large amount of product remaining dissolved in the original amyl alcohol solution from which the emodin monomethyl ether had been separated, as above described, consisted, at least, for the most part, of a mixture of anthraquinone derivatives. Previous experience had shown that the best way to effect a separation of these would be to extract them fractionally by shaking their solutions in ether or chloroform with successive portions of various aqueous alkalis. In the present instance, however, owing to the large amount of material to be dealt with and its sparing solubility in the solvents mentioned, it was necessary, in the first place, to carry out the extraction with the alkalis with the employment of the amyl alcohol solution. This rendered the preliminary separation by no means exact, as the salts of the anthraquinone derivatives are appreciably soluble in amyl alcohol.

The amyl-alcoholic solution was therefore extracted successively with aqueous solutions of ammonium carbonate, sodium carbonate, and potassium hydroxide, each extract being acidified as soon as it was separated.

Isolation of Emodin, $\text{CH}_3 \cdot \text{C}_{14}\text{H}_4\text{O}_2(\text{OH})_3$.

The ammonium carbonate extract yielded a nearly black, amorphous powder, from which nothing definite could be isolated. The sodium carbonate extract, however, gave, on acidification, a yellow powder, which, after being crystallised three times from pyridine, yielded 19 grams of a product crystallising in deep orange-coloured needles. On exposure to the air, or on heating, this compound readily lost pyridine, after which it melted at 252° , and was identified as emodin. (Found, $\text{C}=66.5$; $\text{H}=3.9$. Calc., $\text{C}=66.7$; $\text{H}=3.7$ per cent.) Its identity was further confirmed by its conversion into triacetylmodin, which formed slender, pale yellow prisms, melting at 192° .

Tribenzoylmodin, $\text{CH}_3 \cdot \text{C}_{14}\text{H}_4\text{O}_5\text{Bz}_3$.—Emodin was benzoylated by Oesterle (*Arch. Pharm.*, 1899, 237, 703) and by Tschirch and Heuberger (*loc. cit.*), but these investigators obtained only a

dibenzoyl derivative (m. p. 225°). The product of the benzylation of emodin, as obtained by the present authors, consisted, however, entirely of *tribenzoylmodin* (m. p. 186°).

Emodin was benzyolated by the Schotten-Baumann method, and the product crystallised from glacial acetic acid. Small, nodular masses, consisting of minute, pale yellow needles, were thus obtained which melted at 186° :

0.1034 gave 0.2804 CO_2 and 0.0366 H_2O . $\text{C}=74.0$; $\text{H}=3.9$.

$\text{C}_{36}\text{H}_{22}\text{O}_8$ requires $\text{C}=74.2$; $\text{H}=3.8$ per cent.

Isolation of Rheinolic Acid, $\text{C}_{16}\text{H}_9\text{O}_4\cdot\text{CO}_2\text{H}$.

The pyridine mother liquors from the emodin were concentrated, and the solution then poured into a quantity of ether. This caused a product to be precipitated, which, on examination, proved to be rhein, together with some amorphous material. The ethereal filtrate was then extracted with an aqueous solution of ammonium carbonate, when, on acidifying the alkaline liquid, a reddish-coloured powder was precipitated. This product was collected, and crystallised several times from pyridine, when dark red, lustrous needles were obtained, which, on drying at 130° , lost pyridine, and then melted at $295\text{--}297^{\circ}$, previously changing slightly at 290° :

0.1086 gave 0.2613 CO_2 and 0.0329 H_2O . $\text{C}=65.6$; $\text{H}=3.4$.

0.0748 „ 0.1797 CO_2 „ 0.0244 H_2O . $\text{C}=65.5$; $\text{H}=3.6$.

$\text{C}_{17}\text{H}_{10}\text{O}_6$ requires $\text{C}=65.8$; $\text{H}=3.2$ per cent.

This substance is therefore seen to be a new compound, possessing the formula $\text{C}_{17}\text{H}_{10}\text{O}_6$, and it is proposed to designate it as *rheinolic acid*, with consideration of the fact that it is a carboxylic acid, and also contains at least one hydroxyl group. Rheinolic acid is rather more soluble in the usual solvents than is rhein, and it is also of a much more pronounced red colour than the latter. Its homogeneity was confirmed by converting it into its acetyl derivative, which, after several recrystallisations, was hydrolysed, when rheinolic acid was regenerated, possessing the same properties as before its acetylation. *Acetylrheinolic acid* crystallises in rosettes of small, orange-coloured needles, which melt at 236° . It quickly dissolves in cold aqueous sodium carbonate, thus indicating the presence of a carboxyl group.

Rheinolic acid is evidently an anthraquinone derivative, as it dissolves in both alkalis and concentrated sulphuric acid with an intense red colour, but differs from rhein, inasmuch as it is not reprecipitated by the addition of water to its dilute solution in the latter solvent. Rheinolic acid is probably related structurally to rhein, but since it differs from the latter by the increment of the

elements C_2H_2 , it probably contains a bridged ring. Further quantities of rheinolic acid were subsequently isolated from the tarry product precipitated by the addition of petroleum to the ethereal extract of the aqueous liquid (p. 957), and also from the ethereal extract of the resins (p. 965), but the total amount obtained did not greatly exceed 0.3 gram.

There were some indications that the mother liquors from the emodin, from which the rheinolic acid had been isolated, contained yet another substance in small amount, but it could not be isolated.

Isolation of Aloe-emodin, $C_{14}H_5O_2(OH)_2 \cdot CH_2 \cdot OH$.

On acidifying the potassium hydroxide extract of the amyl-alcoholic solution, obtained as above described, a yellow product was precipitated. This was dissolved in chloroform, when, on keeping, a quantity (1.5 grams) of a substance separated. This separated from ethyl acetate in long, highly lustrous needles of a light brownish-orange colour, which melted at 216° , and proved to be aloe-emodin. (Found, $C=66.4$; $H=4.0$. Calc., $C=66.7$; $H=3.7$ per cent.) Its identity was further confirmed by the preparation of its triacetyl derivative, which crystallised well in pale yellow needles, but decomposed somewhat indefinitely from 165° to 175° (Found, $C=63.3$; $H=4.1$. Calc., $C=63.6$; $H=4.0$ per cent.), and its tribenzoyl derivative melting at 232° (compare Robinson and Simonsen, *loc. cit.*). Aloe-emodin is removed from its solution in chloroform or ether somewhat slowly by fairly concentrated sodium carbonate solution, but is much more quickly extracted by the alkali hydroxides.

Aloe-emodin has not previously been recorded as a constituent of rhubarb, but no doubt can be entertained that the "rhabarberon" of Hesse and the "isoemodin" of Tschirch and Eyken, both of which melted at 212° , were, in reality, aloe-emodin in a state of approximate purity. Hesse, however, in one communication (*J. pr. Chem.*, 1908, [ii], 77, 383) describes both "rhabarberon" and aloe-emodin, and evidently regarded them as distinct substances.

Isolation of Chrysophanic Acid, $CH_3 \cdot C_{14}H_5O_2(OH)_2$.

The chloroform solution from which the aloe-emodin had separated, as above described, was extracted with several successive portions of 0.5 per cent. aqueous potassium hydroxide. This treatment removed further quantities of aloe-emodin, and when this compound ceased to be extracted the strength of the alkali employed was increased to 5 per cent. The deep purple-red, alkaline extracts then obtained yielded, on acidification, a quantity (6 grams) of a

yellow powder, which was found to consist of a mixture of emodin monomethyl ether (about one part) and chrysophanic acid (about four parts). As no pure substance could be isolated from this product by crystallisation, it was heated at 160° with concentrated sulphuric acid in order to demethylate the emodin monomethyl ether. The product was then dissolved in chloroform and extracted with aqueous sodium carbonate, which removed emodin, after which it was shaken with aqueous potassium hydroxide, which dissolved the chrysophanic acid.

The product obtained on acidifying the last-mentioned alkaline extract was crystallised from ethyl acetate, when chrysophanic acid was obtained in deep golden-coloured spangles, melting at 191° . (Found, C=70.9; H=4.0. Calc., C=70.9; H=3.9 per cent.) It yielded diacetylchrysophanic acid, which formed slender, pale yellow prisms, melting at 204° .

Dibenzoylchrysophanic Acid, $\text{CH}_3 \cdot \text{C}_{14}\text{H}_5\text{O}_4\text{Bz}_2$.—Chrysophanic acid was benzoylated by the Schotten-Baumann method, and the resulting product crystallised from a mixture of glacial acetic acid and alcohol. *Dibenzoylchrysophanic acid* was then obtained in very pale yellow needles, melting at 204° :

0.1119 gave 0.3084 CO_2 and 0.0400 H_2O . C=75.2; H=4.0.

$\text{C}_{29}\text{H}_{18}\text{O}_6$ requires C=75.3; H=3.9 per cent.

Isolation of Gallic Acid.

The tarry product which was precipitated by the first addition of petroleum to the ethereal extract of the aqueous liquid (p. 950) was heated with a large volume of ether, when only partial solution was effected. The undissolved portion was therefore dissolved in alcohol, the solution poured into the ethereal liquid, and the mixture washed several times with water. This caused the separation of a quantity of brown, tarry matter, which yielded nothing crystalline. The aqueous-alcoholic washings which had been separated from the ethereal solution and from the tar were evaporated to a low bulk under diminished pressure, and extracted many times with ether. The ethereal liquid thus obtained was extracted successively with aqueous solutions of ammonium carbonate, sodium carbonate, and potassium hydroxide. The last two extracts yielded only small quantities of emodin and aloe-emodin respectively, but on acidifying the ammonium carbonate extract and again extracting with ether, gallic acid, crystallising from water in colourless needles, was obtained. This, after being dried at 130° , melted and decomposed at 253° . (Found, C=49.3; H=3.8. Calc., C=49.4; H=3.5 per cent.) Its identity was confirmed by its conversion into trimethyl-

gallic acid, which melted at 165° . The melting point of gallic acid is usually recorded as about 220° , but the present authors were unable to cause any specimen of gallic acid to fuse at so low a temperature unless it were partly decomposed by prolonged heating above 200° .

Gallic acid has once previously been stated to occur in rhubarb (Tschirch and Heuberger, *loc. cit.*), but no experimental evidence was recorded.

The original ethereal liquid from which the gallic acid had been removed by washing with water was extracted with various alkalis, and very fully examined. It yielded only small quantities of gallic and cinnamic acids, rhein, rheinolic acid, emodin, aloë-emodin, emodin monomethyl ether, chrysophanic acid, and an amorphous, tarry product. The total amount of gallic acid isolated from the ethereal extract of the aqueous liquid was about 20 grams, but a much larger quantity was subsequently obtained.

Isolation of a Mixture of Glucosides of the Anthraquinone Derivatives.

The original aqueous liquid (A), which had been extracted with ether, as previously described, was deprived of this solvent, and extracted in portions with amyl alcohol. Each portion was extracted twenty-five times, and, owing to the large volume of liquid, this necessitated nearly 1000 operations. Each amyl-alcoholic extract of the aqueous liquid, after being washed with water, was evaporated to a low bulk under diminished pressure. The first extract obtained from each portion of aqueous liquid, on evaporation, yielded a quantity of brown, tarry matter, but all the subsequent extracts, when sufficiently concentrated, deposited a brown, granular solid. The entire amount of the latter was dried on porous earthenware, after which it was digested with ethyl alcohol, in which it was only sparingly soluble, even on boiling. The product, which was at first amorphous, gradually assumed a crystalline form, and when this change was complete the mixture was filtered and the solid washed with alcohol. In this way a quantity (130 grams) of a bright yellow, crystalline solid was obtained. The filtrate from the latter was dark reddish-brown, and contained only tarry matter similar to that yielded by the first extractions with amyl alcohol.

The yellow, crystalline solid was insoluble, or practically so, in xylene, ether, chloroform, or ethyl acetate, sparingly soluble in alcohol, and very sparingly so in water, but it dissolved much more readily in glacial acetic acid, pyridine, or solutions of the alkali

hydroxides. With the latter, or with dilute pyridine, it yielded a deep purple-red colour. It separated in an amorphous state from all solvents other than ethyl alcohol.

A quantity (10 grams) of the yellow, crystalline product was dissolved in glacial acetic acid, and the solution poured into 9 litres of boiling water. Such an amount of sulphuric acid was then added to the solution as would represent one per cent. of the total liquid, after which the mixture was boiled for twenty minutes. A yellow precipitate formed in the boiling mixture after a few moments, and rapidly increased in amount. This was collected, and the aqueous filtrate extracted with chloroform, after which the solid precipitate was digested with the chloroform solution so obtained. The material undissolved by this treatment was found to be rhein (0.8 gram), whilst the chloroform solution, on systematic examination, yielded emodin (2.0 grams), aloe-emodin (0.3 gram), emodin monomethyl ether (1.0 gram), and chrysophanic acid (1.4 grams). The aqueous liquid from which the above-mentioned anthraquinone derivatives had been separated was colourless. It was deprived of sulphuric acid by means of barium hydroxide, and evaporated to a low bulk. A quantity of a syrup was thus obtained, which was found to contain dextrose. It was converted into the osazone, and the latter carefully examined for rhamnosazone (compare, Perkin, *Trans.*, 1910, **97**, 1777), when it was found to consist entirely of *d*-phenylglucosazone (m. p. 213°). These results prove that the yellow, crystalline product was a mixture of the glucosides of rhein, emodin, aloe-emodin, emodin monomethyl ether, and chrysophanic acid, and it probably also contained a small percentage of the glucoside of rheinolic acid.

With the endeavour to isolate an individual glucoside from this mixture, a quantity of the material was fractionally crystallised many times from alcohol. A product was eventually obtained which formed highly lustrous, bright yellow leaflets, which melted constantly at 235° , and appeared quite homogeneous. Although some separation had been effected, it was, however, still a mixture, for, on hydrolysis, in addition to dextrose, chrysophanic acid and emodin monomethyl ether were obtained. It is not surprising that the glucosides of these two substances should be inseparable, since the substances themselves cannot be separated by crystallisation. This inseparable mixture of the glucosides of emodin monomethyl ether and chrysophanic acid contained one molecule of alcohol of crystallisation :

0.1548, on heating at 130° , lost 0.0154 EtOH. EtOH=9.9.

0.0853 * gave 0.1848 CO_2 and 0.0399 H_2O . C=59.1; H=5.2.

* Anhydrous substance.

$C_{21}H_{20}O_9$, EtOH requires EtOH = 9.9 per cent.

$C_{22}H_{22}O_{10}$, EtOH „ EtOH = 9.3 „ „

$C_{21}H_{20}O_9$ requires C = 60.6; H = 4.8 per cent.

$C_{22}H_{22}O_{10}$ „ C = 59.2; H = 4.9 „ „

A further attempt to separate the original mixture of glucosides was made by the recrystallisation of the sodium derivative from very dilute alcoholic sodium hydroxide, but only a partial separation, similar to that just described, could be effected. Various other methods were also tried, but all were equally unsuccessful.

As a final attempt to isolate an individual glucoside, a portion of the original mixture was acetylated, when an acetyl derivative was obtained, which crystallised in pale yellow needles. This acetyl derivative was crystallised many times from glacial acetic acid and from ethyl acetate, after which it melted somewhat indefinitely at about 190°, but, on hydrolysis with dilute acid, it was found that no appreciable separation had been effected.

The dark reddish-brown, tarry product contained in the first amyl-alcoholic extracts and in the original amyl-alcoholic filtrates from the crude mixture of glucosides was deprived of solvent as completely as possible by evaporation under diminished pressure, and the residue dissolved in alcohol. An equal volume of chloroform was then added to the warm solution, whereupon a large amount of a dark-coloured, resinous product was precipitated. This material is subsequently referred to as the product (a). The liquid decanted from this precipitated resin was evaporated to a low bulk, and then largely diluted with chloroform, with which it was heated for some time. This caused the separation of a large amount of a yellow, granular solid. The latter, which is subsequently referred to as the product (b), was collected, washed with chloroform, and dried. The chloroform filtrate from the product (b) was evaporated to a low bulk, and then largely diluted with ether. The small precipitate produced by this treatment yielded nothing definite, and the ethereal filtrate was added to the original ethereal extract of the aqueous liquid (A)

Examination of the Product (a).

The product (a), which amounted to about 1000 grams, was heated with water, when it entirely dissolved, but the greater part of the material separated again on cooling as a brown resin. The dark-coloured aqueous liquid which had been decanted from the brown resin was treated with basic lead acetate solution, which removed some amorphous colouring matter. The filtrate from the lead precipitate was then examined for glucosides soluble in water,

but was found to contain only a little sugar. The resin, which was sparingly soluble in cold water, represented, as stated in the introductory part of this paper, the chief purgative principle of the rhubarb, but nothing definite could be directly isolated from it. A quantity (30 grams) of this material was dissolved in boiling water, a solution of potassium hydroxide added, and the mixture boiled for one minute. The liquid was then poured into hydrochloric acid, and extracted with ether. The greater part of the material was undissolved by the ether, and formed a pitch-like mass, but on systematically examining the ethereal liquid, small amounts of cinnamic and gallic acids, emodin, and aloe-emodin were obtained. These compounds had evidently been present in the resin in the form of esters, or some analogous compound, since a control experiment showed that the glucosides of the anthraquinone derivatives were not decomposed by the treatment with alkali to which the resin had been subjected, and, moreover, cinnamic acid could not yield a glucoside, since it contains no hydroxyl group. Several previous investigators have stated that rhubarb contained a "glucoside" which gave gallic and cinnamic acids on hydrolysis, but it is evident that the relatively small proportions of these acids which do not occur in the free state in rhubarb are combined as esters.

Isolation of a New Compound, $C_{14}H_9(OH)_3$.

A further portion of the above-described resin was dissolved in hot water, and such an amount of sulphuric acid added as to represent 3 per cent. of the total liquid, which was then heated on a water-bath for one hour. The mixture was then cooled, and the aqueous liquid decanted from the pitch-like mass which had separated, and extracted with ether. The ethereal liquid was then extracted with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide. The products dissolved by the first-mentioned alkali were gallic and cinnamic acids, and rhein, whilst the potassium hydroxide extract yielded only aloe-emodin, emodin monomethyl ether, and chrysophanic acid. The sodium carbonate extract, however, was found to contain a new substance, together with a large proportion of emodin. The product obtained on acidifying the sodium carbonate extract was redissolved in ether, and extracted with successive portions of dilute sodium carbonate solution until all the emodin had been removed. The strength of the alkali was then increased, when, on acidifying the alkaline extracts, the new substance was obtained. This compound was crystallised from dilute alcohol, when it formed long, flattened needles of a pale brown colour, which melted at 256° :

0.1012 gave 0.2719 CO_2 and 0.0485 H_2O . $\text{C}=73.3$; $\text{H}=5.3$.

0.1040 „ 0.2801 CO_2 „ 0.0501 H_2O . $\text{C}=73.5$; $\text{H}=5.4$.

$\text{C}_{14}\text{H}_{12}\text{O}_3$ requires $\text{C}=73.7$; $\text{H}=5.3$ per cent.

This compound is evidently new, since it does not agree in its properties with any substance of the above formula which has previously been described. It is sparingly soluble in water, but very readily so in alcohol. It yields no colour with ferric chloride, nor, at first, with potassium hydroxide solution, but when dissolved in the latter the mixture gradually becomes yellowish-brown. Concentrated sulphuric acid dissolves the new compound with a yellow colour.

As shown below, this new compound contains three hydroxyl groups, and it is probably a *trihydroxydihydroanthracene*, since, when a small quantity of its acetyl derivative was oxidised by means of chromic acid, and the product hydrolysed, a preparation was obtained which yielded colours with potassium hydroxide and with sulphuric acid similar to those afforded by some anthraquinone derivatives. The amount of material available, however, did not admit of the nature of the substance being conclusively proved.

A small quantity of the trihydroxy-compound was acetylated by means of acetic anhydride, when a *triacetyl* derivative was obtained, which crystallised from ethyl acetate in colourless needles, melting at 113° :

0.0975 gave 0.2422 CO_2 and 0.0468 H_2O . $\text{C}=67.7$; $\text{H}=5.4$.

$\text{C}_{14}\text{H}_9\text{O}_3(\text{CO}\cdot\text{CH}_3)_3$ requires $\text{C}=67.8$; $\text{H}=5.1$ per cent.

The formation of this triacetyl derivative proves the presence of three hydroxyl groups in the substance from which it was prepared.

The original acid aqueous liquid, from which the above-described compound and the mixture of anthraquinone derivatives had been removed by means of ether after the hydrolysis, was examined, but nothing definite could be isolated from it. It contained no sugar, thus proving that the resin which had been hydrolysed contained nothing of a glucosidic nature.

Examination of the Product (b).

The product (b), which amounted to about 318 grams, was dissolved in 600 c.c. of amyl alcohol, and 3 litres of ether were added. This caused the precipitation of a brown resin, from which the liquid was decanted. The latter was then evaporated, and the precipitation with ether repeated, after which the same operations were performed for a third time. The precipitated resin so obtained was similar in character to that yielded by the product (a). The ethereal liquid which had been decanted from the resin, when

evaporated, gave a product which, on crystallisation from water, yielded a large amount of gallic acid. The aqueous filtrate from the latter was saturated with ammonium sulphate, when a quantity (about 50 grams) of a tarry product was precipitated. The aqueous liquid decanted from this tar was extracted with ether, when it yielded a trace of anthraquinone derivative, together with gallic acid. The total amount of gallic acid obtained from the product (b) was about 190 grams.

The tarry product which had been precipitated by the addition of ammonium sulphate was moderately soluble in water, and was the only product obtained which exhibited the properties of a tannin. It was freed from the last traces of gallic acid by being precipitated a second time with ammonium sulphate. A quantity of this tannin was then heated with dilute sulphuric acid, when it was converted, for the most part, into a resinous product. The latter was moderately soluble in water, but differed from the original tannin inasmuch as it did not precipitate gelatin. The treatment of the tannin with sulphuric acid also led to the formation of small amounts of gallic and cinnamic acids, a mixture of anthraquinone derivatives, and a dextrorotatory sugar which yielded *d*-phenylglucosazone (m. p. 211°).

A portion of the original aqueous liquid (A), which had been extracted with ether and with amyl alcohol, was treated with a solution of basic lead acetate, when a comparatively small, reddish-coloured precipitate was produced. This, when decomposed by hydrogen sulphide, yielded a dark brown liquid, which gave a blackish-green colour with ferric chloride, but contained no tannin, and nothing could be directly isolated from it.

A portion of the product obtained on decomposing the lead precipitate was dried, and examined for acids, such as malic acid, by esterification with ethyl alcohol, but with a negative result. Another portion of the material was heated with dilute aqueous sulphuric acid, after which the mixture was extracted with ether. During this operation a small amount of sparingly soluble matter separated in the lower part of the ethereal layer. The ethereal liquid contained only traces of gallic acid and anthraquinone derivatives, but the sparingly soluble solid crystallised from pyridine in brown, flattened needles, which did not melt at 340°. A further small quantity of this substance was subsequently isolated from the ethereal extract of the resin (B), but the total amount obtained was not sufficient for analysis. It gave an acetyl derivative, which crystallised from acetic anhydride in pale brown needles, melting at 335°.

Isolation of Dextrose.

The filtrate from the basic lead acetate precipitate was deprived of lead, and concentrated, when it formed a viscid, yellow syrup. This was kept for several weeks, when it gradually deposited a considerable quantity of crystals, which were identified as dextrose.

A quantity of the sugar was heated with acetic anhydride and a little camphorsulphonic acid, after which the mixture was shaken with water and then extracted with ether. The ethereal solution, after being washed with aqueous sodium carbonate, was evaporated, when Tanret's " α -penta-acetyldextrose" * was obtained. This product, after recrystallisation from 95 per cent. alcohol, formed colourless needles, melting at 127—128°. This method of preparation of this acetyldextrose is more expeditious, and gives much better yields than that recommended by Tanret (*Compt. rend.*, 1895, 120, 194). The syrup from which the dextrose had been isolated was levorotatory, as was also the original syrup before the separation of the dextrose. It gave no indication of containing anything other than levulose.

Examination of the Resin (B).

The resin (B) amounted to 414 grams. It was mixed with prepared sawdust, and extracted successively in a large Soxhlet apparatus with petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol. In order to ensure as complete a separation of the products as possible, the different extracts were then submitted to extraction in the reverse order, as follows: The alcohol extract was again mixed with sawdust, and extracted with ethyl acetate; this new ethyl acetate extract, together with the original one, was then mixed with sawdust, and extracted with chloroform; and so on, until all but the petroleum extract had been treated a second time. Each extract was finally removed from the sawdust by a suitable solvent. This second extraction effected a very considerable change in the amounts of some of the extracts.

Examination of the Petroleum Extract.

The petroleum extract of the resin was a dark greenish-brown, viscid liquid, and amounted to 72 grams. It was treated with ether, in which all but a small amount of emodin monomethyl ether dissolved. On extracting the ethereal liquid with aqueous ammonium carbonate, a small amount of rhein was removed, after

* It has more recently been shown (Koenigs and Knorr, *Ber.*, 1901, 34, 957) that this compound is more correctly designated as the β -derivative.

which the ethereal solution was shaken with several successive portions of potassium carbonate solution. The material precipitated on acidifying the potassium carbonate extracts, after being freed from a little resinous matter and an amorphous product which caused the formation of emulsions, was heated with absolute alcohol containing some sulphuric acid, in order to esterify the acids which it contained. The mixture was then poured into water, the esters extracted with ether, and freed from a small amount of emodin by means of caustic alkali. These esters of the free fatty acids, which amounted to 17 grams, were distilled under diminished pressure, and examined, together with a similar product obtained from the combined acids.

The original ethereal liquid which had been extracted with potassium carbonate, as above described, was shaken with aqueous potassium hydroxide. This removed about 4 grams of a mixture consisting of aloë-emodin, emodin monomethyl ether, and chrysophanic acid. The ethereal solution of the neutral products was then evaporated, and the residual fatty matter heated with an excess of alcoholic potassium hydroxide.

Isolation of Verosterol, $C_{27}H_{46}O$.

The liquid obtained by the above saponification was poured into water and extracted with ether, when an oily product was obtained which deposited a quantity of flattened needles. As this solid did not appear homogeneous, and could not be purified by distillation under diminished pressure or by recrystallisation, it was heated with acetic anhydride. The product, after being freed from a small quantity of a hydrocarbon (m. p. 64°), yielded verosteryl acetate, melting at 118° :

0.0602 gave 0.1791 CO_2 and 0.0622 H_2O . $C=81.1$; $H=11.5$.

$C_{27}H_{45} \cdot O \cdot CO \cdot CH_3$ requires $C=81.3$; $H=11.2$ per cent.

On hydrolysis this acetate yielded verosterol (Power and Rogerson, *Trans.*, 1910, **97**, 1951), which was identified by analysis and by determination of its rotatory power. The original filtrate from the crude verosterol contained, besides a further amount of this substance, only an uncrystallisable oily liquid of high boiling point.

Identification of the Fatty Acids.

The alkaline aqueous liquid which had been extracted with ether, as above described, was acidified, and the liberated acids, none of which were volatile in steam, extracted with ether and converted into their ethyl esters. The product was distilled under diminished pressure, when it amounted to 11 grams. For the

examination of the fatty acids, these esters, together with the similar product previously obtained from the free acids, were hydrolysed, and the resulting acids converted into their barium salts. The resulting salts were digested with a mixture of benzene (95 parts) and 94 per cent. alcohol (5 parts), according to Vongerichten's method (*Ber.*, 1909, **42**, 1638). After cooling the mixture, the undissolved salt was collected, and the acid regenerated. The product so obtained was crystallised from ethyl acetate several times, when it melted at 54—57°, and was found to be a mixture of palmitic and stearic acids. (Found, C=74·7; H=12·5 per cent. Acid value, 211·2.) Palmitic and stearic acids have acid values of 218·8 and 197·2 respectively.

The barium salts remaining dissolved in the mixture of benzene and alcohol were treated with hydrochloric acid, and the resulting unsaturated fatty acids (16·2 grams) distilled under diminished pressure. This product had an iodine value of 134·8, and when oxidised according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, Vol. I, 360) it yielded about equal quantities of di- and tetra-hydroxystearic acids, and a very small amount of linusic acid. The unsaturated fatty acids therefore consisted of about equal quantities of oleic and linolic acids, together with a small amount of linolenic acid.

Examination of the Ether, Chloroform, Ethyl Acetate, and Alcohol Extracts.

The ethereal extract amounted to 217 grams. It was very fully examined by fractionally extracting with various alkalis, in a manner analogous to that previously described in connexion with the ethereal extract of the aqueous liquid (p. 953). It yielded rhein, rheinolic acid, emodin, aloë-emodin, emodin monomethyl ether, and chrysophanic acid, together with a small amount of the sparingly soluble substance melting above 340° (p. 962), and a little free verosterol.

The chloroform extract of the resin amounted to 4·6 grams. A portion of it (1·2 grams) was extremely sparingly soluble in chloroform, and was found to consist of a mixture of the glucosides of emodin monomethyl ether and chrysophanic acid. The more readily soluble portion yielded chiefly rhein and emodin, together with small amounts of the other anthraquinone derivatives.

The ethyl acetate extract of the resin was a dark-coloured powder, and amounted to 72·5 grams. It consisted to a considerable extent of a mixture of the glucosides of rhein, emodin, aloë-emodin, emodin

monomethyl ether, and chrysophanic acid, similar to that previously described (p. 957), together with a black, amorphous powder.

The alcoholic extract of the resin was a hard, black solid, and amounted to 33 grams. Nothing crystalline could be separated from it, but on hydrolysis with acid it yielded small amounts of emodin monomethyl ether and chrysophanic acid.

Physiological Tests.

The physiological action of many of the products obtained from rhubarb was investigated, the results in nearly all cases being controlled by experiments on several individuals. The doses administered were in all cases 0.1 gram.

Of the anthraquinone derivatives, rhein, emodin, and emodin monomethyl ether were found to be devoid of purgative action, the first two compounds being quickly excreted in the urine. Aloe-emodin and chrysophanic acid, however, were distinctly purgative, although not very active.

The crystalline mixture of glucosides of the anthraquinone derivatives had a bitter, astringent taste, but was quite devoid of purgative action.

The non-glucosidic resin obtained from the product (a) of the amyl alcohol extract of the aqueous liquid had a prompt purgative action, 0.1 gram causing a much more pronounced effect than the same weight of aloe-emodin or of chrysophanic acid, although it represented a much smaller amount of the drug.

The tannin from the product (b), and the alcohol extract of the resin (B), appeared to be quite devoid of physiological action.

Summary.

The results of the present investigation may be summarised as follows:

The material employed consisted of the best quality of sun-dried "Shensi" rhubarb.

An alcoholic extract of the drug, when distilled with steam, yielded small amounts of palmitic and chrysophanic acids, together with a hexoic acid and some essential oil.

The portion of the extract which was soluble in water yielded cinnamic and gallic acids, rhein, emodin, aloe-emodin, emodin monomethyl ether, chrysophanic acid, and a new anthraquinone derivative, $C_{17}H_{10}O_6$ (m. p. 295—297°), which it is proposed to designate *rheinolic acid*. It yielded, furthermore, a crystalline mixture of glucosides of rhein, emodin, aloe-emodin, emodin monomethyl ether, and chrysophanic acid; dextrose; lævulose; tannin;

and an amorphous, non-glucosidic resin, which represents the chief purgative constituent of the drug. This resin, on hydrolysis, gave small amounts of gallic and cinnamic acids, rhein, emodin, aloë-emodin, emodin monomethyl ether, and chrysophanic acid, together with a new compound, $C_{14}H_{12}O_8$ (m. p. 256°), which is probably a *trihydroxydihydroanthracene*, and a large amount of resinous material.

The portion of the extract undissolved by water yielded a trace of a hydrocarbon (m. p. 64°); a phytosterol (verosterol), $C_{27}H_{46}O$; a mixture of fatty acids, consisting of palmitic, stearic, oleic, linolic, and linolenic acids, both free and combined; rhein; rheinolic acid; emodin; aloë-emodin; emodin monomethyl ether; chrysophanic acid; and a trace of a substance which did not fuse at 340° , but which yielded an acetyl derivative, melting at 335° . It also gave some amorphous products, and a further quantity of the crystalline mixture of glucosides of the anthraquinone derivatives.

Of the anthraquinone derivatives, only aloë-emodin and chrysophanic acid had any purgative action, the mixture of glucosides being quite inert. The chief purgative principle is the above-mentioned non-glucosidic resin.

The percentages of the more important products obtained in the course of the present investigation may be indicated as follows, although the figures represent only approximately the amounts of the various substances actually present in rhubarb:

Essential oil, 0.005; verosterol, 0.1; mixture of fatty acids, 0.31; cinnamic acid (free), 0.01; gallic acid (free), 2.2; rhein, 0.12; rheinolic acid, 0.003; emodin, 0.78; aloë-emodin, 0.16; emodin monomethyl ether, 0.22; chrysophanic acid, 0.49; non-glucosidic resin, 10.4; tannin, 0.52; crystalline mixture of glucosides of the anthraquinone derivatives, 2.0.

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C.—The Occurrence of Alizarin in Rhubarb

By HUGO MÜLLER.

DURING the course of an investigation of rhubarb root carried out many years ago (*Jahresber.*, 1857, 517), Warren de la Rue and the author succeeded in isolating from this root emodin and chrysophanic acid. At a later date the author acquired a quantity of the residue which accumulates during the preparation of the

official aqueous extract of rhubarb, and this was extracted in a large copper extraction apparatus with benzene, and the extract fractionally crystallised from the same solvent. During this process it was noticed that a substance was present which dissolved in alkalis with a blue colour, and was much less soluble in benzene than either emodin or chrysophanic acid. Careful investigation has now shown that this substance is alizarin. The dark orange, crystalline mass remaining after the removal of the emodin and chrysophanic acid by benzene was crystallised from tetrachloroethane,* in which it was sparingly soluble in the cold, and from which it separated as a beautiful microcrystalline mass of orange needles:

0.1200 gave 0.3096 CO_2 and 0.0364 H_2O . $\text{C}=70.3$; $\text{H}=3.4$.

$\text{C}_{14}\text{H}_8\text{O}_4$ requires $\text{C}=70.0$; $\text{H}=3.3$ per cent.

That this substance is alizarin was evident from its behaviour on sublimation, and from the fact that, on treatment with lime water and barium hydroxide, it gave precipitates which were exactly similar to those yielded by alizarin under the same conditions. Comparative dyeings carried out with this substance and pure alizarin gave also identical results. In order that there could be no doubt that the substance from rhubarb was alizarin, it was converted, by digesting with sodium acetate and acetic anhydride, into the diacetyl derivative, which, after repeated crystallisation from acetic acid, melted at $186\text{--}187^\circ$, which is somewhat higher than the melting point of diacetylalizarin previously observed ($179\text{--}183^\circ$: Perkin, *Trans.*, 1899, **75**, 448). When, however, a very pure specimen of sublimed alizarin was acetylated under the same conditions, and the product repeatedly recrystallised from acetic acid, the diacetylalizarin obtained was also found to melt at $186\text{--}187^\circ$, and it was furthermore observed that there was no alteration in melting point when the latter preparation was mixed with the diacetylalizarin obtained from rhubarb.

Alizarin appears to be contained in rhubarb only in very small quantity, and this is no doubt the reason why its presence has, so far, been overlooked.

My thanks are due to Mr. Robert Robinson, of Manchester University, for assistance in connexion with these experiments.

* Tetrachloroethane, which is now manufactured on the large scale, appears to be an excellent solvent for the purification, not only of alizarin, but also of other hydroxyanthraquinones and allied substances.

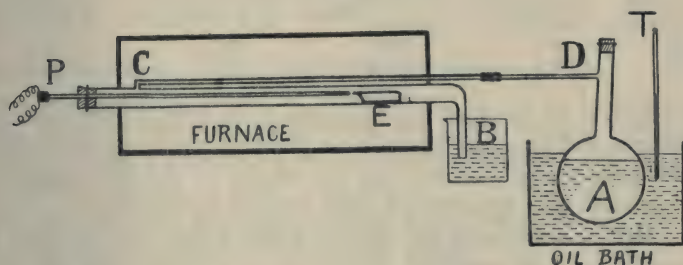
CI.—*The Action of Steam on Iron at High Temperatures.*

By JOHN ALBERT NEWTON FRIEND, THOMAS ERNEST HULL, and
JOSEPH HALLAM BROWN.

FOR more than a century it has been known that, when steam acts on iron at high temperatures, ferroso-ferric oxide is produced with the simultaneous liberation of hydrogen. It has recently been shown (Friend, *J. Iron and Steel Inst.*, 1909, ii, 172; *J. West Scotland Iron and Steel Inst.*, 1910, 17, 66) that this reaction probably takes place in three stages, namely:

- (1) The dissociation of the steam.
- (2) The combination of the nascent oxygen with iron to form ferrous oxide, at approximately 350° .

FIG. 1.



- (3) The further oxidation of the ferrous oxide to ferroso-ferric oxide, Fe_3O_4 .

It occurred to us that if a quantitative study were made of the rate at which iron is oxidised by steam at different temperatures, the point at which ferroso-ferric oxide began to form might be determined.

To this end some pure iron wire was heated to redness in a current of pure hydrogen, and ultimately cooled in as perfect a vacuum as could be obtained with a mercury pump. In this way any traces of oxide were reduced, and occluded gases expelled. The wire was now hammered out to a thickness of approximately 0.05 mm., and weighed into a porcelain boat. This was now placed in a silica tube *BCD*, of the shape shown in Fig. 1, and heated in an ordinary gas furnace. Flask *A*, which contained dilute potash solution, was heated to boiling in an oil-bath steadily maintained at 120° , and as the steam had to pass through the narrow

silica tube *DC*, and then through *CE* before reaching the boat, it had a good opportunity of arriving at the temperature of the iron before reaching the same. The temperature was determined by means of the platinum resistance pyrometer *P*, which was checked from time to time, and found to be quite trustworthy.

The reaction between the steam and the iron could be followed in two ways, namely, by collecting the hydrogen evolved, and by noting the increase in weight of the iron. It was to be expected that the former method would yield results slightly too low, owing to the solubility of the gas in water and to the presence of traces of air in the apparatus.

In order to determine how closely the two methods might be made to agree, several experiments were carried out, in which the increase in weight of the iron and the volumes of hydrogen gas evolved were severally determined. The results of two of these are given in the following table, and may be regarded as typical:

Temperature of iron.	Duration (hours).	Increase in wt. of iron, gram.	Equivalent vol.* of hydrogen at N.T.P., c.c.	Vol. of hydrogen collected, at N.T.P., c.c.
750°	5.5	0.0265	37.1	36.3
820	7.5	0.0275	38.5	36.5

The figures in the last two columns show only a very moderate agreement, and since, in addition to yielding more accurate results, a determination of the increase in weight of the iron was most easily carried out, we adopted that method exclusively.

In order to determine the rate at which steam acts on iron, the boat containing the weighed metal was introduced into the silica tube, through which steam was passing, and already raised to about 200—300°, at which temperatures Friend has shown the steam to have no action on the metal. The temperature was now rapidly raised to that desired, and maintained constant. After a certain time the furnace was rapidly cooled to about 150°, the boat drawn out, and slipped into a glass tube containing calcium chloride and immediately evacuated, to prevent the possibility of any further oxidation and to remove any traces of steam. On cooling, the increase in weight was noted. The results are given in the following table, and are shown graphically in Fig. 2.

* This is calculated from Morley's results, namely, that 1000 c.c. of oxygen at N.T.P. weigh 1.42900 grams (*Zeitsch. physikal. Chem.*, 1897, 20, 68).

Temperature.	Duration of expt., hours.	Initial wt. of iron, gram.	Increase in wt., gram.	Wt. of oxygen combined with 100 grams of iron.*
500°	1·0	0·1842	0·0104	5·64
500	3·0	0·1842	0·0130	7·05
500	7·0	0·1842	0·0170	9·22
650	2·5	0·1350	0·0188	13·92
650	10·5	0·1350	0·0422	31·26
650	12·5	0·1350	0·0430	31·85
650	20·5	0·1350	0·0438	32·44
720	2·0	0·0864	0·0224	25·92
720	8·0	0·0864	0·0292	33·79
720	10·5	0·0864	0·0306	35·41
720	13·0	0·0864	0·0309	35·76
720	20·0	0·0864	0·0315	36·45
820	1·0	0·1610	0·0555	34·47
820	3·0	0·1610	0·0585	36·33
820	5·0	0·1610	0·0611	37·95
820	6·0	0·1610	0·0611	37·95
950	0·5	0·1808	0·0464	25·66
950	1·0	0·1808	0·0649	35·89
950	1·5	0·1808	0·0678	37·50
950	3·0	0·1808	0·0688	38·05

A consideration of the above results, as shown in Fig. 2, enables us to arrive at the following conclusions:

(1) At 500° the reaction between the steam and the iron is so superficial that a practically infinite time would be required for its completion.

(2) At 820° the reaction proceeds until the whole of the metal has been converted into ferroso-ferric oxide.

(3) At temperatures intermediate between 500° and 820° the curves become practically parallel to the abscissa. At first sight it would appear that this is due to the fact that the outer layers of the metal have been converted into ferroso-ferric oxide, and the process of diffusion is so slow at the temperatures under consideration that a practically infinite time is required for the interior portions to be converted into the same oxide. Such is undoubtedly the explanation when thick pieces of iron are heated in the air, and might apply if thick pieces of iron had been used in the case under discussion, but with metal 0·05 mm. thick and at dull red-heat this is scarcely credible.

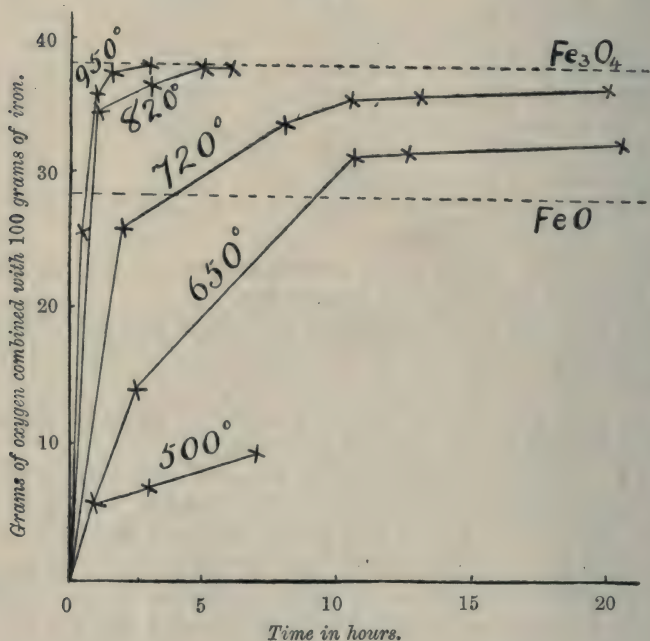
Another explanation is possible. Ferrous oxide has probably a lower dissociation pressure than ferroso-ferric oxide, and is consequently the oxide first formed when steam acts on iron at low

* FeO contains 28·65 grams of oxygen combined with every 100 grams of iron, and Fe₃O₄ contains 38·19 grams of oxygen combined with the same weight of iron. The figures in bold type indicate when this latter state has been reached within the limits of experimental error. The atomic weight of iron is taken as 55·85 (O=16).

temperatures (350°), as Friend in the paper referred to has shown. Probably at this temperature the dissociation pressure of the oxygen of the steam is only very slightly greater than that of the ferrous oxide, but is less than that of the ferroso-ferric oxide. As the temperature rises, so does the oxygen pressure, until at 820° it slightly exceeds that of the ferroso-ferric oxide, and this oxide is accordingly produced.

At temperatures intermediate between 350° and 820° , mixtures of ferrous oxide and ferroso-ferric oxide may therefore be formed,

FIG. 2.



having dissociation pressures in equilibrium with that of the steam at the same temperature. When once this equilibrium has set in, therefore, as indicated by the curves assuming a horizontal direction in Fig. 2, no further oxidation can take place unless the temperature be raised, the very slight increase in weight observed being attributable to experimental error induced by the presence of traces of air in the apparatus. This explanation would be definitely proved to be correct were some ferroso-ferric oxide actually reduced in a current of steam to some such value as that indicated in the curve for 720° or 650° , but we were never able to do it. This failure, however, does not necessarily prove the explanation to be

untenable, for it is well known that many substances undergo considerable change after formation. Thus, Hilpert (*Ber.*, 1909, **42**, 4575) shows that, whereas ferrous oxide which has not been heated above 400° may be reduced in a current of hydrogen at 280° , yet if it has been previously subjected to a temperature of 1200° it cannot be reduced by hydrogen below 330° , indicating that its dissociation pressure has been lowered. Somewhat similar remarks have been shown more recently to apply to the dissociation pressure of cupric oxide by Allmand (*Trans.*, 1910, **97**, 603). Evidently, therefore, the data are insufficient to enable us to say with certainty which of the two explanations is correct, but the balance of evidence appears to be in favour of the theory advocated by the present authors. It was not possible for us to use our apparatus at higher temperatures than 950° , and we cannot therefore say with certainty that ferroso-ferric oxide is the final product of oxidation of iron in steam. A few preliminary experiments apparently indicate that a slightly higher state of oxidation is possible, corresponding, it may be, with Fe_8O_{11} , which has been suggested by Haber and Goldschmidt (*Zeitsch. Elektrochem.*, 1906, **12**, 49) as the composition of the oxide inducing passivity. The research is therefore being continued at higher temperatures with fresh apparatus.

In conclusion, we have pleasure in acknowledging our indebtedness to the Research Fund Committee of the Chemical Society for a grant which has made it possible for us to carry out this research.

THE TECHNICAL COLLEGE,
DARLINGTON.

CII.—*The Constitution of Dehydro- β -naphthol Sulphide and the Interaction of Sulphuric Acid with Aromatic o-Hydroxysulphoxides.*

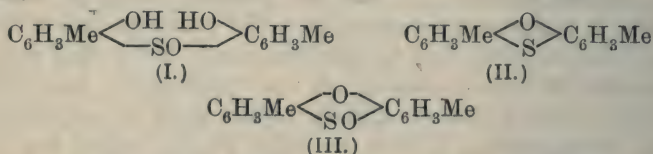
By THOMAS PERCY HILDITCH and SAMUEL SMILES.

PREVIOUS experiments (this vol., p. 408) have shown that prolonged interaction of sulphuric acid with the sulphoxides of *p*-cresol and *p*-chlorophenol yields the oxides of the corresponding phenothioxins. It has also been observed that these substances are not primary products, but are formed from some unstable substances which occur in an earlier phase of the interaction. The experiments described in the present paper deal with these initial products.

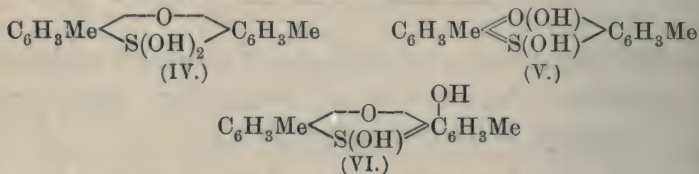
When cold sulphuric acid is allowed to react for a few minutes

with the sulfoxides of *p*-chlorophenol and *p*-cresol, pale orange-coloured substances are obtained on mixing the reacting mixture with excess of water. These compounds are very unstable, and are decomposed even by warming with most organic media; but their reactions are sufficiently definite to permit the resolution of their structure. They are isomeric with the original aromatic sulfoxides (I), and are evidently produced from these by some intramolecular rearrangement.

Constitution of the Products.—The constitution of these substances is demonstrated by the following facts. When reduced with zinc dust in glacial acetic acid, good yields of the phenothioxin (II) are formed, whence it is clear that this cyclic arrangement is present:



It is thus merely necessary to determine the mode of attachment of the remaining O_2H_2 to the phenothioxin group. The oxygen cannot be present as phenolic hydroxyl, for in that case a hydroxyphenothioxin would be obtained on reduction, and it must be concluded that that element is attached to the thioxin group. This is supported by the formation of the oxides of phenothioxin (III) in the prolonged interaction of sulphuric acid with these compounds, and at the same time it must be further concluded that at least one oxygen atom is attached to sulphur. It is also evident that both oxygen atoms cannot be attached to sulphur, as in the hydrated thionyl group (IV), for the following reasons:



(1) The substance does not exhibit the normal reaction of the thionyl group.

(2) By interaction with cold aqueous alkali hydroxide the phenothioxins (II) are produced, together with substances of phenolic character. The corresponding sulfoxide (III) does not exhibit this behaviour, and it cannot be supposed that the mere conversion of the thionyl group to the ortho-condition would produce such a profound change in the character of the substance.

(3) Substances of the ortho-type are not obtained from simple aromatic sulfoxides by interaction with sulphuric acid.

The hydrated thionyl structure being thus unacceptable, there remain only two alternatives in accordance with the facts: either that of the thio-oxonium hydroxide (V) or the isomeric form of quinolic character (VI). It is impossible to adduce constructive evidence in favour of one or other of these structures; indeed, it seems highly probable from former work on substances of this type (Hantzsch, *Ber.*, 1899, **32**, 3109; Kehrmann, *Annalen*, 1902, **322**, 31; 1910, **372**, 287; Werner, *Ber.*, 1901, **34**, 3300) that the two are interchangeable, the former being preferred in acid media in the form of a salt, and the latter in neutral or in the free condition. Finally, bearing in mind the general instability of oxonium hydroxides, we consider that preference must be given to the quinolic structure.

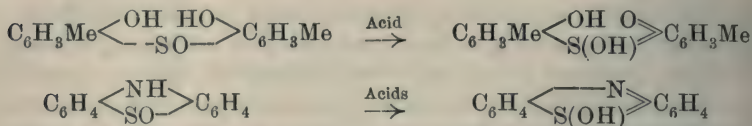
The chief characteristics of these substances may be summed up as follows:

- (1) Reduction yields the phenothioxins.
- (2) The phenothioxins are also produced by interaction with aqueous alkali hydroxide, but here phenolic derivatives are simultaneously formed.
- (3) Prolonged interaction with sulphuric acid yields the oxides of the phenothioxins.
- (4) They are of weakly basic character; the dimethyl derivative (VI) furnishes a platinichloride, which is decomposed by hydrolytic agents.
- (5) They are not very stable substances, for when heated alone in certain solvents they appear to undergo simultaneous reduction and oxidation, phenothioxin and phenolic derivatives being formed.

Formation of the Products.—It has been previously recorded (this vol., p. 409) that the sulfoxides of *p*-cresol and *p*-chlorophenol are readily converted by sulphuric acid into the oxides of the corresponding phenothioxins, whereas this and other dehydrating agents do not act similarly with the sulphides of those phenols. Hence it was suggested that with sulphuric acid the process is not primarily one of simple dehydration, and this view is now fully confirmed by the isolation of these initial products in which the phenothioxin system has been formed without loss of water. Moreover, from this notable difference in the behaviour of the sulphides and sulfoxides it seems probable that at some stage or other the thionyl group is indirectly concerned in the formation of the thioxin system.

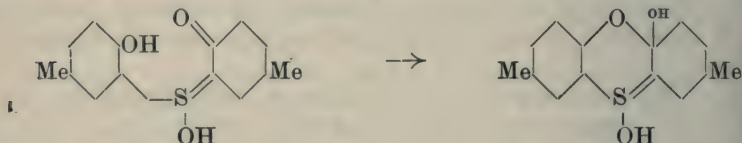
At any rate, it is clear that these preliminary products are formed by some intramolecular rearrangement of the di-*o*-hydroxy-thionyl structure, and from what has been observed of the influence of acids on the *o*-sulfoxides of diphenylmethane (Hilditch and Smiles, this vol., p. 145) and diphenylamine (Barnett and Smiles, *Trans.*, 1910, **97**, 186, 1112, 1559) there can be but little doubt

that the first stage in this change is the production of the sulphonium quinone:



The *o*-sulphoxides of diphenylmethane and diphenylamine are very readily converted by sulphuric acid into the sulphonium quinones as above indicated, and since all the mechanism necessary to this change (this vol., p. 151, and Barnett and Smiles, 1910, **97**, 194) is present in the di-*o*-hydroxysulphoxides, there is every reason to suspect that it will now take place. There is, moreover, further reason in support of this assumption, for it will be shown later that in the naphthalene series a substance containing the quinonoid sulphonium structure of this type may be isolated, and it is very easily converted into the naphthathioxin derivative.

Assuming, then, the formation of the sulphonium quinone, the conversion of that substance into the phenothioxin is seen to follow by a simple intramolecular transposition which involves the union of the phenolic with the quinonoid nucleus:



It may not be out of place to remark that this type of union is to be found in many other cases, for example, the formation of quinhydrone, and although it is not suggested that the cyclic substances in question belong to that class of compound, it is noteworthy that Jackson and Oenslager (*Ber.*, 1895, **28**, 1614) regard their formation in a similar manner.

Dehydro-β-naphthol Sulphide.—It has long been known that when the *α*-sulphide of *β*-naphthol,* $\text{HO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{S} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, is treated with alkaline oxidising agents it loses two atomic proportions of hydrogen, and is converted into a stable, scarlet substance, which has been termed dehydro-*β*-naphthol sulphide. Onufrowicz (*Ber.*, 1890, **23**, 3358) prepared this compound from the sulphide with mercuric oxide or with an ammoniacal solution of silver oxide, whilst Henriques (*Ber.*, 1894, **27**, 2999) employed an alkaline solution of potassium ferricyanide (see also Schiller-Wechsler,

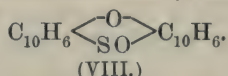
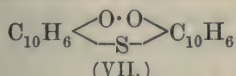
* For the orientation of this substance, see Henriques (*loc. cit.*) and Mauthner (*Ber.*, 1906, **39**, 1340).

D.R.-P. 64816). We have found that it may also be obtained from di- β -naphthol sulphide with an alkaline solution of iodine.

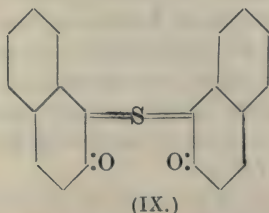
A very thorough investigation of this substance was made by Henriques (*loc. cit.*), and the chief results may be summed up as follows:

- (1) It is formed from β -naphthol sulphide by removal of two atoms of hydrogen.
- (2) It has the simple molecular weight corresponding with the sulphide.
- (3) It is not attacked by aqueous alkali hydroxide.
- (4) When reduced, it yields a naphthol sulphide; this is not identical with the original sulphide, but is easily converted into the latter by warming the alkaline solution, and it may be re-oxidised to the dehydro-compound.
- (5) Phenylhydrazine yields a dihydrazone.

We have confirmed the more important of these results. Henriques discussed several formulæ for this substance, and concluded in favour of the peroxide structure (VII), the only other of importance being that of the naphthathioxin oxide (VIII):



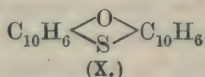
The evidence which he employed in rejecting the latter has since been fully confirmed, for this substance has been prepared by Mauthner (*Ber.*, 1906, **39**, 1340) and by ourselves (this vol., p. 414), and it is not identical with the dehydronaphthol sulphide. Finally, Henriques considered that the conception of the peroxidic structure (VII) was all the more acceptable, since it was in accordance with the hypothesis that the two β -naphthol sulphides are stereoisomerides. It is evident that reduction of the peroxide would yield a sulphide in which the hydroxyl groups are spacially proximate, the more stable form of the sulphide being one in which these groups are further removed from one another. There is, however, another alternative structure for dehydro- β -naphthol sulphide which has not yet been considered; it is that of a sulphonium quinone:



and further examination of the behaviour of the substance shows

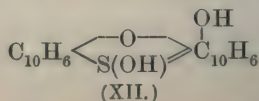
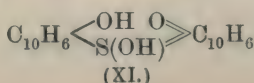
that this is preferable to the peroxide formula. As, indeed, Henriques observed, the dehydro-compound furnishes a diphenylhydrazone, but it must be admitted that if it were a true peroxide of this type it should, on the other hand, preferably yield the naphthol sulphide under the reducing action of the phenylhydrazine. It is true that the substance liberates iodine from an acidified solution of potassium iodide, but since this reaction is exhibited by quinones as well as peroxides it cannot be adduced in favour of either structure. The apparent advantage possessed by the peroxide formula in explaining the production of a stereoisomeric naphthol sulphide is equally shared by the sulphonium-quinone structure. It is beyond the scope of the present paper to discuss the question whether these two sulphides are really stereoisomerides, but if this should prove to be the case—and it appears probable—it is readily seen on assigning a tetrahedral configuration to the quinonoid sulphur that reduction may lead to an isomeric form of the naphthol sulphide.

In conclusion, attention may be drawn to the information which the behaviour of this substance gives with regard to the hypothesis advanced in the previous portion of this paper. In this connexion the most interesting property of the β -naphthasulphonium-quinone is the interaction with alcoholic alkali hydroxide; naphthathioxin (X) is then formed, together with other products of phenolic



character, the process probably being one of simultaneous oxidation and reduction. Similar behaviour is shown by the products (VI) obtained from the interaction of sulphuric acid with the sulphoxides of *p*-cresol and *p*-chlorophenol; but here the process is of a less complex nature, for the thioxin system is already present in these compounds.

Nevertheless, it is clear that the behaviour of this naphthalene derivative shows how easily the sulphonium-quinone structure of that type may be converted into the thioxin arrangement, and this is the essential condition of the hypothesis in question. In fact, this interaction with alkali hydroxide can only be explained by assuming that β -naphthasulphoniumquinone (IX) absorbs the elements of water, yielding the sulphonium hydroxide (XI), which then undergoes further rearrangement into the thioxonium derivative (XII), this in turn being finally attacked by the alkali, yielding the naphthathioxin (X):



The results of this discussion are summed up as follows:

(1) The interaction of sulphuric acid with the di-*o*-hydroxy-sulphoxides in question first yield the quinonoid sulphonium compounds (type IX).

(2) This suffers further change, and is converted into the phenothioxonium derivative (type VI).

(3) Confirmatory evidence is shown by the behaviour of dehydro- β -naphthol sulphide, which is more correctly to be termed β -naphthasulphoniumquinone. Naphthathioxin is formed from this substance by interaction with alcoholic sodium hydroxide.

EXPERIMENTAL.

Derivatives of 2:7-Dichlorophenothioxin.

p-Chlorophenol-*o*-sulphoxide, in quantities of about 2 grams at a time, was triturated with cold concentrated sulphuric acid. The solution was kept at the atmospheric temperature for about fifteen minutes, and then poured into ice-cold water, when a bright orange-coloured precipitate formed. This was collected, and washed with cold water until free from sulphuric acid. The material was further purified by dissolving it in cold methyl alcohol or acetone, and allowing the solvent partly to evaporate. 2:7-Dichlorophenothioxonium hydroxide was then obtained in pale orange-coloured plates, which melted at 142–145°:

0.1040 gave 0.1827 CO₂ and 0.0246 H₂O. C=47.9; H=2.6.

0.1163 „ 0.2081 CO₂ „ 0.0306 H₂O. C=47.9; H=2.8.

C₁₂H₈O₃Cl₂S requires C=47.52; H=2.64 per cent.

It is essential to the success of this preparation that the sulphoxide employed should be pure.

When the substance is heated in the steam-bath it decomposes, and in further illustration of its instability the effect of boiling solvents may be mentioned. After remaining dissolved in cold acetic acid for twenty-four hours, the substance was recovered unchanged (Found, C=47.2; H=3.1), but after being boiled with that solvent for half an hour, 2:7-dichlorophenothioxin was obtained (m. p. 134°; Found, C=54.1; H=2.0). At the same time a considerable quantity of other products were formed; these were soluble in aqueous alkali hydroxide. A similar decomposition was observed when the solution in ethyl alcohol was boiled; 2:7-dichlorophenothioxin (m. p. 135°; Found, C=54.0; H=2.8. Calc., C=53.5; H=2.23 per cent.) and other products soluble in alkali were obtained.

Interaction with Reducing Agents.—Two grams of the substance were reduced in acetic acid solution with zinc dust, and when interaction was complete the filtered solution was mixed with water.

The precipitate was collected, and treated with dilute aqueous alkali hydroxide, which removed a very small quantity of soluble material. The insoluble residue was recrystallised from alcohol, when slender needles of 2:7-dichlorophenothioxin were obtained (m. p. 135°).

Interaction with Sulphuric Acid.—A cold solution in this medium was set aside for some hours, and then poured into cold water. After purification, the precipitate yielded 2:7-dichlorophenothioxin oxide in colourless, blunt prisms, which melted at 166°. (Found, C=50·8; H=2·2. Calc., C=50·5; H=2·1 per cent.)

Interaction with Sodium Hydroxide.—The substance was triturated with a cold dilute aqueous solution of sodium hydroxide. After the lapse of twelve hours the insoluble material was collected, washed with water until free from alkali, and then crystallised from alcohol. 2:7-Dichlorophenothioxin was obtained in long, colourless needles (m. p. 135°; Found, C=53·57; H=2·6 per cent.).

An attempt was made to ascertain the nature of the products which were soluble in alkali. These were recovered from the alkaline filtrates by adding dilute mineral acid, and then recrystallised from dilute alcohol. The less soluble portion melted and decomposed at about 200°, and a sample which had been dried in the steam-oven was analysed:

0·1027 gave 0·1798 CO₂ and 0·0224 H₂O. C=47·76; H=2·4.

The data seemed to indicate that the substance is either the *p*-chlorophenol *o*-sulphoxide (C=47·5; H=2·6) or a hydroxy-derivative of dichlorophenothioxin oxide (C=47·8; H=2·0); but since it is not easy to distinguish between these by analysis, the benzoyl derivative was prepared. This melted at 131—132°, whilst the *dibenzoyl* derivative of *p*-chlorophenol *o*-sulphoxide, which was prepared for comparison, melted at 207°:

0·1980 gave 0·4414 CO₂ and 0·0536 H₂O. C=60·8; H=3·0.

C₂₆H₁₅O₅Cl₂S requires C=60·96; H=3·13 per cent.

The two substances were not identical, but the nature of the compound in question at present remains indeterminate.

An acetic acid solution of phenylhydrazine does not react with this phenothioxonium derivative. Cold acetyl chloride attacks it vigorously with decomposition, whilst benzenesulphinic acid appears to unite with it.

Derivatives of 2:7-Dimethylphenothioxin.

p-Cresol *o*-sulphoxide was treated with cold sulphuric acid as described with *p*-chlorophenol *o*-sulphoxide, but the interaction should not be extended over so long a period, seven to eight minutes

being, in this case, sufficient. The mixture was poured on ice, and, if the preparation had been successfully conducted, the deep pink material which separated could be easily collected, and washed free from sulphuric acid. It is necessary to employ the pure sulfoxide for this preparation, otherwise the product is apt to be difficult to handle. After purification in the manner already described, 2:7-dimethylphenothioxonium hydroxide was obtained in orange leaflets, which melted indefinitely at 105—110°:

0.1013 gave 0.2378 CO₂ and 0.0476 H₂O. C=54.03; H=5.22.

C₁₄H₁₄O₃S requires C=64.12; H=5.34 per cent.

The substance is less stable than the corresponding dichloro-derivative. It furnished a *platinichloride* as a buff-coloured powder and a *picrate* of a greenish-brown colour; analysis of these showed that they were partly hydrolysed.

Reduction of the substance in cold acetic acid was effected with zinc dust. When the mixture had become colourless, it was collected, the filtrates being then mixed with water. An oil was precipitated, but it soon solidified, when the material was collected, and recrystallised from light petroleum. 2:7-Dimethylphenothioxin was thus obtained in soft, colourless leaflets (m. p. 71°; Found, C=73.38; H=5.4. Calc., C=73.69; H=5.26 per cent.).

Interaction with alkali was studied in a similar manner to that described with the dichloro-compound. The portion insoluble in the alkaline reagent consisted of 2:7-dimethylphenothioxin (m. p. 71°; Found, C=72.9; H=4.8), whilst the phenolic compounds obtained by acidifying the filtrates were of indefinite nature. Benzenesulphinic acid unites with this substance as with the dichloro-derivative.

Dehydro- β -naphthol Sulphide or β -Naphthasulphoniumquinone.

This substance was prepared several times from β -naphthol sulphide by Henriques' method, employing an alkaline solution of potassium ferricyanide. After being crystallised from acetic acid, the substance formed scarlet prisms, which melted at 156°. It was also prepared by adding a solution of the requisite amount of iodine in aqueous potassium iodide to a solution of the sulphide in excess of aqueous sodium hydroxide. The precipitate was collected, dried, and purified from acetic acid, when a substance was obtained, which melted at 158°. These samples were analysed:

0.1882 gave 0.5214 CO₂ and 0.0622 H₂O. C=75.53; H=3.67.

0.1472 „ 0.4120 CO₂ „ 0.0530 H₂O. C=76.33; H=4.00.

C₂₀H₁₂O₂S requires C=75.95; H=3.8 per cent.

(Henriques found m. p. 155°; C=76.12; H=4.19.)

The *hydrazone* was also prepared by adding phenylhydrazine to a warm solution of the substance in acetic acid, according to the method described by Henriques. It was obtained in orange leaflets, which melted at 182° :

0.1145 gave 0.3232 CO_2 and 0.0503 H_2O . $\text{C}=76.98$; $\text{H}=4.88$.

0.2504 „ 24.4 c.c. N_2 at $17^{\circ}/771$ mm. $\text{N}=11.47$.

Henriques found $\text{C}=77.78$; $\text{H}=5.0$; $\text{S}=6.66$; whilst:

$\text{C}_{32}\text{H}_{24}\text{N}_4\text{S}$ requires $\text{C}=77.42$; $\text{H}=4.84$; $\text{N}=11.29$;

$\text{S}=6.45$ per cent.

The quinone liberates iodine from an acidified solution of potassium iodide; it was isolated by solution in carbon disulphide.

Interaction with Alkali Hydroxide.—The substance was boiled for half an hour with a concentrated alcoholic solution of sodium hydroxide. The sparingly soluble yellow residue was crystallised from hot alcohol, when a yellow, crystalline powder was obtained. It melted at 166° , whether alone or mixed with naphthathioxin from other sources. (Found, $\text{C}=79.62$; $\text{H}=4.3$. Calc., $\text{C}=80.00$; $\text{H}=4.00$ per cent.) At least half of the quinone was converted into phenolic derivatives which were soluble in alkali. Products of definite composition were not isolated from this mixture.

Interaction with Concentrated Sulphuric Acid.—The method employed was the same as that described with β -naphthol sulphide (this vol., p. 415). The product was repeatedly crystallised from acetic acid; but it was purified with difficulty. Finally, a yellow, crystalline powder was obtained, and this was evidently naphthathioxin oxide, for it melted at about 220° . (Found, $\text{C}=76.3$; $\text{H}=3.98$. Calc., $\text{C}=75.95$; $\text{H}=3.80$ per cent. M. p. 221° : Hilditch and Smiles, this vol., p. 415; m. p. 220° : Mauthner, *Ber.*, 1906, **39**, 1340.)

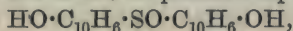
Since the oxidation of β -naphthol sulphide in alkaline solution yields the sulphonium-quinone, and not the expected sulfoxide, we have endeavoured to prepare the latter substance in order to examine the relations between the two compounds. The reagent employed was hydrogen dioxide, which has been found to be particularly suitable for the preparation of sulfoxides and sulphides (Gazdar and Smiles, *Trans.*, 1908, **93**, 1833; Hinsberg, *Ber.*, 1908, **41**, 2836).

Oxidation of β -Naphthol Sulphide in Neutral Solution.—A solution of the sulphide in acetone was mixed with concentrated hydrogen dioxide in slight excess of the amount required to form the sulfoxide. After the lapse of four to five days the mixture was poured into water, and the red precipitate was collected, washed, dried, and then redissolved in acetone, from which it was

fractionally precipitated with light petroleum. The less soluble portion yielded a small quantity of a sandy, crystalline material, whilst the more soluble consisted of red needles, which melted indefinitely at 105—110°. The melting point and composition of this substance (C=73·5; H=4·2 per cent.) were not altered by recrystallisation from acetic acid. Although the analytical data from the product of this reaction do not appear to correspond with any simple compound, some evidence of the nature of the substance may be gathered from the interaction with reducing agents.

Reduction was effected with zinc dust in glacial acetic acid. The product, after being crystallised from this solvent, formed a yellow, crystalline powder, which melted at 165°, whether alone or mixed with a sample of naphthathioxin. (Found, C=79·5; H=5·1. Calc., C=80·0; H=4·0 per cent.) It thus appears probable that the product in question is similar to the thioxonium derivatives obtained from the simpler sulphoxides and sulphuric acid.

In any case it is clear that β -naphthol sulphoxide,



if, indeed, it is capable of existence, is not a very stable substance, and tends to pass into the diquinone (IX) by loss of water, or into the monoquinone (XI), and thence into the thioxin derivative (XII) by intramolecular rearrangement. With the sulphoxides of *p*-cresol and *p*-chlorophenol we have not been able to produce the former change, whilst sulphuric acid is necessary for the latter.

Many other attempts to prepare the sulphoxide of β -naphthol were without success. However, the dibenzoyl derivative was obtained in small amounts and under special conditions.

Dibenzoyl- β -naphthol sulphide was prepared in the usual manner. It melts at 208°, and is sparingly soluble in most cold organic media:

0·1037 gave 0·2945 CO₂ and 0·0391 H₂O. C=77·4; H=4·19.

C₃₄H₂₄O₄S requires C=77·57; H=4·18 per cent.

This was treated with hydrogen dioxide in warm acetic anhydride solution; the majority of the substance was recovered unchanged, but from the portion which was most soluble in acetic acid a small amount of a pale yellow, crystalline substance was obtained. This melted at 160°, and from the analytical data appears to be *dibenzoyl- β -naphthol sulphoxide*:

0·1802 gave 0·4954 CO₂ and 0·0692 H₂O. C=74·98; H=4·27.

C₃₄H₂₄O₅S requires C=75·26; H=4·06 per cent.

The substance dissolves in sulphuric acid with a deep blue colour. The investigation of these and similar substances is being continued.

In conclusion, we desire to thank the Research Fund Committee of the Society for a grant which has defrayed the expenses of this research.

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CIII.—*Apparatus for the Maintenance of Constant Pressures Above and Below the Atmospheric Pressure. Application to Fractional Distillation.*

By JOHN WADE, D.Sc., and RICHARD WILLIAM MERRIMAN, M.A.

IN planning a series of quantitative fractionations under reduced and increased pressures, it became evident that extensive modifications would be required in the appliances at present available for these purposes. The introduction of the evaporator column by Young (*Trans.*, 1899, **75**, 679) has converted the formerly crude process of fractional distillation into an operation as precise as any in chemistry, and attention must now be given to differences in boiling point, pressure, and relative yield that twenty years ago would have been regarded as beyond the limit of experimental error. For both high and low pressures an efficient pressure regulator is essential. Arrangements must be made to furnish a steady supply of air at pressures above the normal. The admission of air to the distilling flask required to prevent bumping under low pressures calls for a special device when the flask is surmounted by a heavy fractionating column. Means must be contrived for protecting a sensitive thermometer from abnormal pressures without diminishing its sensitiveness or introducing lag. Finally, some device is needed for changing the receiver at frequent intervals without disturbing the pressure, or incurring appreciable loss by evaporation.

I. *A New Pressure Regulator, or Manostat.*

Probably the most efficient pressure regulator hitherto available is that of the late Sir W. H. Perkin (*Trans.*, 1888, **53**, 689). It consists essentially of a glass air inlet valve, which is actuated by an electromagnet, the circuit of which is completed automatically whenever the mercury in a manometer tube makes contact with an adjustable platinum wire. But as those who are familiar with this instrument are aware, it cannot be relied on to work continu-

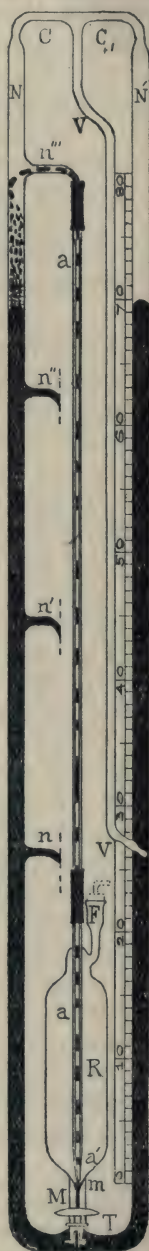
ously for any extended period; sooner or later it fails because of the fouling of the mercury by sparks from the platinum wire. And as in conducting a fractionation through a long column the operator is already fully occupied, if attention were liable to be distracted by the need of re-starting the regulator there would be risk of missing some important change in the boiling point.

After considering various alternatives it was perceived that a suitable instrument might be constructed which would admit air on the principle of a mercury thermostat. The regulating mechanism of a thermostat consists essentially of a gas inlet passage, which is automatically left uncovered by the mercury of a thermometer when the temperature falls below the limit to which the instrument is set. The analogous device for regulating pressure should accordingly consist of an air inlet passage which is automatically left uncovered by the mercury of a manometer when the pressure falls below this limit. The instrument described below, which may appropriately be termed a *manostat* ($\mu\alpha\nu\acute{o}\varsigma$, thin, attenuated; $\sigma\tau\alpha\tau\acute{o}\varsigma$, stationary), embodies this principle.

The manostat consists of an open syphon manometer (Fig. 1), the long, wide limbs, NN' , of which (10 mm. bore) are united at the top by a smaller cross-tube C . The short limb leads through a short, stout capillary tube M (2 mm. bore) into a bulb R , which is large enough to contain the whole of the mercury needed to fill the long limbs to the full barometric height (130 c.c.). The air inlet tube a (2.5 mm. bore) is sealed into the upper part of the bulb, and drawn out at its lower end into a slender cone a' , which projects into a corresponding funnel-shaped enlargement m of the capillary tube M . The bore of this cone must not exceed 1 mm., and in order to hinder adhesion of the mercury, its apex is truncated at an acute angle with the axis.

The upper end of the air inlet tube is connected through caoutchouc joints and a suitable length of similar tubing a with one or other of four side-tubes, n, n', n'', n''' , which are sealed into the branch N of the manometer; for each particular pressure

FIG. 1.



that tube is selected which is next above the required level of mercury, the other three being closed for the time being by short lengths of thick-walled caoutchouc tubing, sealed by stout glass plugs (not shown in the illustration). Mercury is introduced into the apparatus through a funnel F , and withdrawn by means of a glass tap T , its height above the air inlet a' —that is to say, the negative pressure—being read on a millimetre scale. The tap should be secured by nickel or platinum wire. The general dimensions of the apparatus may be taken from the illustration, in which, however, the calibre of the smaller tubes is exaggerated for the sake of clearness.*

(i) *Arrangement for Low Pressures.*

The distilling apparatus or other system in which a low pressure is required is connected with the upper cross-tube C through a vertical tube V , which is brought to the level of the bulb in order to facilitate manipulation. The manostat is set by exhausting the upper part to a suitable extent, and introducing mercury into the bulb R until the level in the long limbs NN' indicates the required negative pressure; any excess in the bulb is drawn off through the tap. If now this negative pressure is exceeded, the cone a' of the air tube is uncovered by the retreat of the mercury from the funnel m into the capillary M , and the column of mercury in the air tube aa is forced into the upper part of the manometer tube N ; air is consequently admitted until the diminution in negative pressure causes the mercury to rise through the capillary, once more sealing the air inlet.

As the force required to move this mercury column upwards against friction and surface tension (the gravitational forces being balanced) corresponds with a pressure of 2 or 3 mm. of mercury, the negative pressure must be exceeded by that amount in starting the action of the instrument; hence, unless this additional pressure is furnished by blowing gently for a moment into the bulb R (through a tube carried by a caoutchouc stopper in the mouth of the filling funnel F), the initial action from what may be termed a statical equilibrium is somewhat slow and insensitive. Once, however, the column has been set in motion, the peculiar movement of the mercury in the funnel m , due to the rapid increase in its capillary depression † as it retreats into the narrower part of the tube, sets up an intermittent action, and little cylinders of mercury

* Copies of this, and of the other apparatus described in this communication, have been made to the satisfaction of the authors by C. L. Müller, of Parton Street, Kingsway, London, W.C.

† In the 2 mm. tube, 4.5 mm.; in the funnel (3 to 4 mm. diameter), about 2.5 mm.

ascend the air tube in rapid alternation with bubbles of air. The discharge of the mercury into the side-tube N sets up a more massive oscillatory movement in the main column, which, however, being counterbalanced by an opposite oscillatory movement in the compensating tube N' , does not sensibly affect the level in the capillary tube.

The alternating action thus established furnishes what may be termed a dynamical equilibrium, which is remarkably sensitive to alteration in pressure; if the exhaust pump be kept continuously in action, air is admitted at a rate which increases or decreases automatically and almost instantaneously in response to the slightest variation. The sensitiveness and steadiness are at a maximum when the average rate of ascent of the mercury is such that the individual cylinders can just be followed by the eye; with reservoirs (p. 989) of adequate capacity the instrument may be adjusted to maintain any pressure with a maximum deviation of ± 0.2 mm. from the mean.*

In order to secure this, however, two further conditions are essential. In the first place the calibre of the various tubes must not materially depart from the dimensions given. If, for example, the air inlet tube were wider, irregularity would be caused by the cylinders of mercury breaking up and falling back through the air bubbles; whilst if it were sensibly narrower, the increased surface tension would hinder the upward passage of the mercury to an undesirable extent.† In the second place, the mercury must be clean and free from "tail." The method of purification described by Travers (*Study of Gases*, p. 16), in which air is drawn for twenty-four hours or more through the metal while covered with a layer of dilute nitric acid, gives an excellent product. For the same reason it is advisable at the outset to introduce 1 or 2 c.c. of 20 per cent. sulphuric acid into the bulb R ; this is at once taken up into the manometer tube N , and automatically cleanses the mercury while the instrument is in action. Nitric acid is unsuitable, owing to the formation of basic salts.

(ii) *Arrangement for High Pressures.*

As the manostat acts whenever the difference in pressure between the air in the bulb R and the upper part exceeds that to which the

* The actual pressure is, of course, subject also to any fluctuations in the atmospheric pressure (see p. 991).

† The limits of the internal diameter of the air tube have been found by trial to be 2.4 and 2.6 mm. Mercury is carried up even in a 3.0 mm. tube, but above 2.6 mm. the ascent ceases to be regular; below 2.4 mm. it is difficult to dislodge the column which forms when the instrument is started, besides which the action is liable to stop without obvious cause.

instrument is set, it is equally well adapted to the regulation of pressures above atmospheric pressure. In this case the vessel in which the pressure is to be regulated is connected with the bulb *R*, whilst the upper part, through the tube *V*, is left open to the atmosphere. The manostat having been set by means of a vacuum pump as described above, the caoutchouc stopper of the filling funnel *F* is secured by wire, and connexion made with the bulb through the bent tube. As with low pressures, the starting is conveniently accelerated artificially, in this case by temporarily withdrawing air from the upper part of the instrument through the vertical tube *V*.

With the general dimensions given, total pressures up to 1500 or 1600 mm. are readily maintained, the differential pressure indicated on the scale *S* now being positive. Higher pressures could be provided for by increasing the height of the manometer tubes *NN'* and the capacity of the bulb *R* in proportion, as it has been found by trial that mercury in tubes of the dimensions given can be raised to twice or even three times this height (compare Air Compressor, p. 991). It is doubtful, however, whether ordinary glass laboratory vessels could safely be used under such conditions.

If the supply of compressed air is abundant, as when, for example, it is provided by a small mechanical force-pump, the action of the manostat is as free as it is under reduced pressure. If, however, the supply is more limited, as with the mercurial compressor described below, it is necessary to throttle both the air inlet tube into the funnel *F* and the air exit tube *a* by means of screw clamps applied to thick-walled caoutchouc joints (see footnote, p. 994). Ordinary red vulcanised tubing, 2 mm. in internal and 6 to 8 mm. in external diameter, may safely be used up to 1500 mm. pressure without other protection than that afforded by wiring the joints.

As already mentioned, the manostat was devised primarily for use in fractional distillation. It is obviously applicable, however, to any other purpose for which a constant pressure is required, such as the plotting of the vapour pressure curves of highly purified liquids; the maintenance of constant temperatures by Ramsay and Young's boiling-point method (Trans., 1885, 47, 640); and, in conjunction with a protective device described below (p. 995), for the comparison of thermometers at any desired temperature.

II. *Application of the Manostat to Fractional Distillation.*

Although the manostat may be attached directly to the distillation apparatus, the local fluctuations in pressure, due to variations in the action of the water-pump and irregularities in boiling, are too rapid and irregular to permit of the maximum control. In addition to this, the alternate increase and decrease in the volume of the system when the receiver is changed entails a corresponding temporary alteration in pressure, which is only restored to the normal when the excess of air has been removed by the pump, or the temporary deficiency restored by the compressor. The volume of the distillation apparatus rarely exceeds 1000 c.c.; consequently, the change even of a 20 c.c. receiver entails an alteration of 2 per cent. in the pressure.

This is by no means desirable, even temporarily, at high pressures, and at low pressures may be accompanied by a relatively enormous displacement of boiling point; with ordinary alcohol, for example, under 100 mm. pressure, the change would be 0.4° . Moreover, while the manostat simply slows up temporarily in response to a fall in pressure of 0.1 or 0.2 mm., whether negative or positive, at about 2 mm. it stops abruptly, unless, indeed, its sensitiveness be reduced by increasing the size of the air inlet cone a' ; and, as already explained, even a temporary stoppage should be avoided if the efficiency is to be kept at a maximum. This last difficulty might be obviated by exhausting or charging the receiver by means of a separate pump before opening connexion with the rest of the apparatus; but this course would not obviate the other difficulties, and experience has shown that the introduction of a second pump may lead to awkward mistakes.

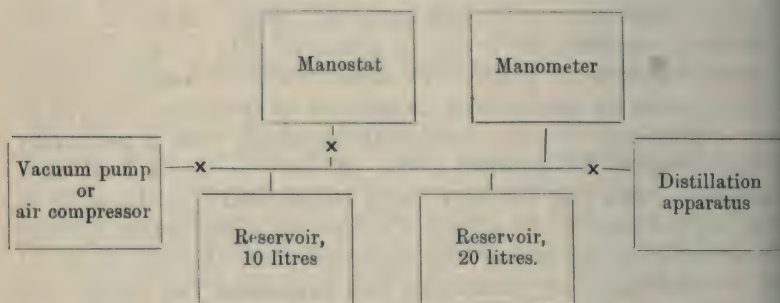
As, however, these irregularities are comparatively small in absolute magnitude, and depend for their importance on the volume of the whole system, they can be reduced to any desired extent by the simple expedient of increasing this total volume. Hence it is advisable to interpose comparatively large reservoirs between the pump and manostat, and between the manostat and distillation apparatus. It has been found by trial that the best results are obtained when the second reservoir has double the capacity of the first; the first vessel eliminates irregularities in the working of the pump, the second those due to the other two causes; for the special work for which the manostat was designed, reservoirs of 10 and 20 litres in respective capacity were employed.

The reservoirs may, of course, consist of single vessels of sufficient strength to withstand the heavy strain to which they are subjected. A very convenient arrangement, however, is that of a series of 2.5 litre bottles ("Winchester quarts"), having unground necks

provided with well-fitting caoutchouc stoppers. The stoppers carry wide T-pieces (5 mm. bore), which are connected in series by short lengths of thick-walled red caoutchouc tubing; if the stoppers and tubing are moistened with very dilute alkali before final adjustment, they soon form permanently vacuum-tight joints. For pressures above the atmospheric pressure, the stoppers and caoutchouc joints must be secured by wire, the joints further, as a precautionary measure, being strengthened by wrapping with adhesive linen tape. Ordinary "Winchester quarts" may be evacuated without risk of collapse, or charged to two atmospheres above atmospheric pressure (that is, a total internal pressure of 2250 mm. of mercury) without risk of bursting; it is well, however, as a precautionary measure, to guard the bottles by means of wire screens similar to those employed in filling mineral water bottles.

The general arrangement of the whole apparatus is indicated in the following diagram:

FIG. 2.



General arrangement of apparatus for fractional distillation at pressures other than atmospheric pressure. (The crosses indicate screw clamps on caoutchouc joints, by means of which the sections of apparatus indicated may be cut off from the reservoirs and manometer.)

The manometer consists preferably of an elongated open U-tube about 5 mm. in bore, which is secured to a board in contact with a silvered glass millimetre scale. The limbs are conveniently about 90 cm. long; one of them is left permanently open to the atmosphere, dust being excluded by means of a loose filter of cotton-wool; the other is provided with a narrowed termination, to which the caoutchouc connexion with the reservoirs may be attached. The difference in pressure from that of the atmosphere being given by the difference in level of the two columns, the actual pressure in the system is obtained by subtracting this from or adding it to the current barometric reading. This arrangement, although involving an additional reading and a little more calculation, is much preferable to any form of closed manometer, for however carefully such an instrument is filled in the first instance, the level

of the mercury is so frequently altered that the introduction of small quantities of air by creeping is practically unavoidable; besides which, a second instrument is then required for pressures above the atmospheric pressure.

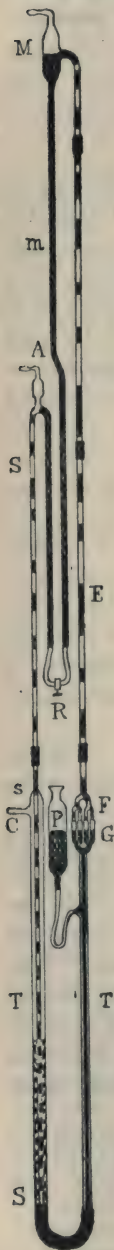
III. *A Mercurial Air Compressor, actuated by an Automatic Sprengel Pump.*

On considering the question of the supply of compressed air in fractional distillation under increased pressure, it appeared desirable to avoid any risk of increasing the pressure to a dangerous extent. Although every part of the apparatus is tested beforehand to a differential pressure at least double the maximum to which it is to be subjected, and the more fragile parts are guarded by wire screens, one can never be quite confident as to the mechanical resistance of glass which has been long exposed to abnormal and varying conditions.* For this reason the idea of utilising a power-driven compression pump, or cylinder of highly compressed air, as the source of air supply, was abandoned; for it was doubtful whether any safety valve could be found which would act sufficiently rapidly to counteract a rapid increase of pressure such as might readily arise from inadvertence or oversight during a long series of fractionations. As it had been decided to limit the excess of pressure to one atmosphere, it seemed probable that air up to this pressure might be obtained by interposing a catch vessel at the base of a Sprengel pump; and it is on this principle that the instrument about to be described is constructed.

Mercury from a reservoir *M* (Fig. 3) passes through a thick-walled capillary tube *m* (2 mm. bore) into a Sprengel fall tube *SS*, air (or other gas), admitted through a safety bulb *A*, being carried down the fall tube in the usual manner. The flow of mercury is controlled by means of a screw clamp *R*, which compresses a short loop of thick-walled caoutchouc tubing of the dimensions and quality already mentioned (p. 988); this need not be reinforced, but it should be bound to the glass by wire. The Sprengel tube is sealed about half-way down into a long U-tube *TT'*, the wider limb, *T*, of which (7 mm. bore) serves as a catch vessel for the air discharged at the bottom. (In order to diminish the risk of fracture, it is convenient to introduce a caoutchouc joint

* The only accidents experienced in the course of upwards of 100 fractionations under increased pressure have been due, in one case, to the cracking of an electrolytically coppered flask along the edge of the protective shield, and, in the other case, to the expansion of the fractionating column against an over-tight clamp. No untoward results followed in either case, the sudden escape of the litre of vapour in the fractionation apparatus, even at 1500 mm. pressure, scarcely approaching an explosion; the consequent discharge of the reservoirs occupies a minute or two.

FIG. 3.



just above the sealed joint *s*.) The mercury remains in the U-tube and the liberated air rises through it and is delivered at a side-tube *C*, which is sealed into the U-tube immediately below the sealed joint.

The mercury overflow from the upper part of the second limb *T'* of the U-tube (4 mm. bore) is returned to the reservoir *M* by means of an elevator *E*, actuated by a vacuum pump which is connected with the upper part of the reservoir *M*. This mercury elevator, the principle of which was suggested by the steady action of the manostat (p. 986), may be described as a Sprengel pump reversed, little cylinders of mercury being forced in rapid succession up the elevator tube *E* (bore 2.8 ± 0.2 mm.) by atmospheric pressure as long as a good vacuum is maintained in the reservoir *M*. If, however, a single mercury inlet were provided at the bottom of the elevator tube, sooner or later an unbroken column of mercury would ascend nearly to the full barometric height, and the action would stop; this difficulty is obviated by branching the end of the elevator tube into a four-pronged fork *F*, which fits loosely into a similar reversed fork *G*, sealed to the upper end of the overflow tube *T'*.

The mercury never rises simultaneously in the four branches of the fork, however carefully they are levelled, and consequently its ascent in one branch of a pair invariably sets up an oscillation which leaves the end of the other branch temporarily uncovered; the cylinder of mercury from the one is therefore followed by a bubble of air from the other. With a good pump, four branches, or, more correctly, two pairs of branches, seem to supply as much mercury as the elevator tube *E* can carry.* As in the manostat, the bore of the tube should not depart from the dimensions given. The oscillatory action is much facilitated by dividing the tube into two or three sections connected by caoutchouc joints as shown in the illustration.

The instrument is both filled and adjusted by means of a reservoir *P*, which is connected through a length of thick-walled caoutchouc tubing with a

* Given an adequate installation of exhaust pumps, the supply of air could be doubled or tripled by duplicating or triplicating the elevator tube and forks.

branch of the overflow tube T' , and is adjustable vertically. In the first place, the reservoir having been raised to its highest position, in which its base is level with the lower extremities of the fork F , the U-tube is supplied with mercury until this level is reached in both limbs. The regulating clamp R being closed (its normal position when the instrument is not in use), the vacuum pump is now started, and more mercury added until the upper reservoir M is filled through the elevator to the level of the side-tube. On now again opening the regulating clamp, the Sprengel pump starts, and all that is necessary in completion is to continue adding mercury cautiously until both elevator and pump are working smoothly.*

The pressure at which the air escapes from the fall-tube exceeds that of the atmosphere by the pressure of the overflow column T' ; it is therefore constant, and equal to the maximum of which the instrument is capable. But as the overflow column is also in equilibrium with the catch-tube column T , the pressure at which the air is finally delivered is measured by the difference in level of the two columns. In starting the instrument after filling, the pressure is, therefore, that of the atmosphere. To adjust the compressor to deliver air at any pressure up to the maximum, all that is necessary is to charge it with compressed air through the delivery tube C until the required difference of level is attained, the reservoir R being lowered to receive the excess of mercury.

Experience has shown, however, that separate adjustment is unnecessary, and that it is more convenient to adjust the instrument when it is connected up with the whole system under control (Fig. 2, p. 990). The manostat having been set to the desired level, air is forced into the reservoirs by means of a compression pump† until the manometer indicates the desired excess, and the manostat is working as rapidly as it would with the corresponding low pressure. Finally, the compressor reservoir P , which at the commencement of the charging with air is placed in its lowest position in order to obviate any risk of accidental overflow from the forked tube G , is raised until the mercury is descending the Sprengel tube at the maximum rate consistent with keeping the upper reservoir M fully charged.

As already indicated, in working with the compressor, the inlet and outlet of the manostat must be throttled until the rate at

* By disconnecting the Sprengel fall tube at the caoutchouc joint, the mercury may be collected in an open trough, from the surface of which it may be raised by the elevator. The compressor may thus readily be utilised as an automatic Sprengel pump; or the whole apparatus may, of course, be constructed to this end.

† A good bicycle hand pump or "foot" pump is ample; reservoirs of the size indicated can be charged to full pressure in a few minutes.

which the mercury passes up the air-tube is not very different from that at which it passes down the Sprengel tube.* With reservoirs of the capacity indicated there is no difficulty in maintaining a pressure of 1500 mm. constant within ± 0.2 mm. If the atmospheric pressure changes during a distillation, the manostat may be readjusted without interrupting the operation, mercury being introduced through one of the side-tubes *n* when necessary; readjustment of the compressor is automatic for small changes.

If a good vacuum be maintained in the reservoir *M*, a compressor of the general dimensions indicated in the illustration (scale one-sixteenth vertically, exaggerated horizontally), and furnished with a single elevator, will supply about 250 c.c. of fully compressed air per minute, or a proportionally larger volume at lower pressures. Should the pressure in the reservoirs from any cause depart from the normal by more than a centimetre, the action at once stops; air alone passing up the elevator if the pressure falls, or a solid column of mercury if the pressure rises. There is thus no risk of mishap. To save re-filling the reservoir *M* when the compressor is started, the regulating clamp *R* should be closed whenever the instrument is stopped.

IV. *Apparatus for Fractional Distillation at Pressures other than the Atmospheric Pressure.*

(i) *Distilling Flask for Reduced Pressures.*

A long fractionating column is a heavy piece of apparatus, and experience has shown that it is undesirable that any part of its weight should be borne by a clamp. In distillation under ordinary or increased pressure ample support is afforded by a stout, round-bottomed flask, resting on stout wire gauze †; but it is difficult, if not impracticable, to pass the necessary capillary air-tube through a caoutchouc stopper.‡ The double-necked flask *D* (Fig. 4), which

* After setting the manostat as previously described, a screw clamp on the lower caoutchouc joint of the air-relief tube *a* (Fig. 1) is tightened (still working under low pressure) until the mercury cylinders pass up the tube at a rate comparable with that at which they pass down the Sprengel tube of the compressor. On now connecting the bulb *R* with the compressed air system, this clamp should not be altered further, but the inlet control clamp on the tube attached to the filling funnel *F* tightened until the action is regularised.

† For distillation under increased pressures, the stopper must be securely wired to the neck of the flask; flasks of Jena resistance glass up to a capacity of 250 c.c. are stable even with two atmospheres in excess.

‡ There does not appear to be a satisfactory substitute for caoutchouc available for this purpose; the only practical course is to expose as little surface as possible

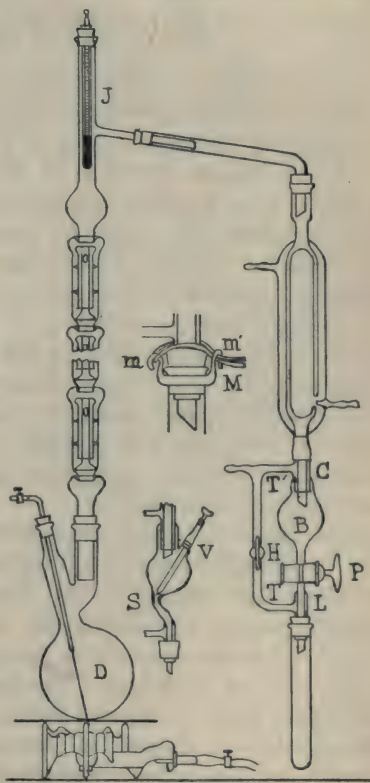
may readily be adapted from an ordinary Claisen flask, has been devised to meet this difficulty. The axes of both necks pass through the centre of the bottom of the spherical portion, so that while the fractionating column which is fitted into the wider vertical neck is still supported under its centre of gravity, a capillary air-tube can be inserted through the bent narrow neck with its point in the centre of the bottom of the flask.

FIG. 4.

(ii) *Protective Jacket for Thermometers.*

The thermometer, which is preferably of Anschütz type, and short enough (15 cm.) to allow the column to be completely immersed in the vapour, is placed in a long, narrow jacket *J* (Fig. 4) of thin-walled tubing, which resembles an elongated test-tube, and is inserted through the caoutchouc stopper in the position usually occupied by the instrument itself. The bore of the tube is as small as is consistent with the free passage of the thermometer without risk of jamming, and its length is such that the whole of the scale appears below the stopper. Thermal contact is afforded by a small quantity of mercury, which with a little care can be adjusted to reach the level of the bottom of the scale; it is essential that the mercury should be well above the top of the bulb; the thermometer must therefore be held down in it, preferably by means of a short length of moderately stout platinum wire.

Comparison under ordinary pressure has shown that the temperatures indicated are identical to 0.01° , whether the instrument is in the jacket or exposed directly to the vapour, and that the natural



to vapours, such as those of ether and chloroform, as are readily absorbed by this material; for this reason, it is advisable to guard all the stoppers by narrow annular spaces, which hinder access of vapour.

lag of the thermometer is not sensibly increased; in other words, the temperature of the mercury-bath under these conditions is identical with the temperature of the saturated vapour. This device enables the thermometer to be changed with so little trouble that its use, even in distillations under atmospheric pressure, is to be recommended.

(iii) *Fractional Separatory Funnels.*

(a) *Reduced Pressure.*—Practically all the fraction separators at present available are based on that of F. D. Brown (Trans., 1878, **35**, 554) or modifications of it by Thorne (Trans., 1883, **43**, 301) or Lothar Meyer (*Ber.*, 1887, **20**, 1833). For quantitative work, however, they have the common defect of liberating a considerable amount of vapour when the receiver is changed; in a well-known variation of Meyer's modification quantitative separation is still further impaired by the accumulation of condensed liquid in the connexions, and its return at a later stage. The modification of Brown's apparatus, shown in the illustration (Fig. 4), is free from these defects, the "loss" being sometimes even less than in a fractionation under ordinary pressure; it has also the advantage that in a slightly less compact form it can be quickly made up from such ordinary appliances as a tap-funnel, adapter, T-pieces and taps or screw clips.

The separator consists essentially of a squat tap-funnel *B*, into the wide neck of which is sealed a sleeve *C* of sufficient calibre to allow the passage of the condenser tube; the latter, which should project well below the sleeve, is made tight by a short length of stout caoutchouc tubing. The tap *P* is preferably of large bore—3 or 4 mm. The stem of the tap-funnel is sealed to the upper end of a second sleeve *L*, the lower end of which carries the caoutchouc stopper of the receiving tube or flask. The two sleeves are respectively furnished with T-tubes *TT'*, the ends of which are sealed to opposite ways of a three-way tap *H*, the third way of which is open to the air. Connexion with the vacuum pump is made through a branch *T''* of the upper side-tube *T*. The working is obvious.

(b) *Increased Pressure.*—The tap *P* of the tap-funnel cannot, as a rule, be lubricated, but as any leakage is inwards, no loss is involved. Under increased pressure, however, a tap is inadmissible, for the leakage is now outwards, whilst the pressure also tends to loosen it. With liquids having no action on vulcanised caoutchouc, a short length of stout pressure tubing provided with a screw-clamp forms an excellent substitute. Where, however, this

is inadmissible, the funnel *B* is provided in lieu of a tap with an internal stopper *S* (inset), which can be actuated from outside.

This stopper is mounted on a stout glass rod, which passes through a closely fitting glass sleeve *V*, to which it is secured by a short length of caoutchouc pressure tubing. The tubing, which is wired to the rod and sleeve, acts as a spring, which normally keeps the stopper away from its embouchure in the upper, bent part of the funnel stem. In changing the receiver, the rod is pressed inwards against the elasticity of the caoutchouc tube until it closes the embouchure; and on relieving the pressure by means of the three-way tap, the stopper is held firmly in position by the pressure of the compressed air in the funnel. Any leakage is downwards and internal, and the receiver can be changed so quickly that considerable oozing may take place without loss.

As already mentioned, in distillation under increased pressure all the caoutchouc joints and stoppers must be wired to the respective glass vessels and tubes. In fractionation under reduced pressure the frictional hold of the caoutchouc stopper of the receiver is reinforced by the upward pressure of the atmosphere, and further support is unnecessary; but with increased pressure, the stopper must be secured mechanically. A convenient fastening is afforded by a stout metal ring *M* (inset), which fits the test-tube fairly closely, and is provided with two stout vertical hooks *mm'*, one of which is radial, and the other parallel to the ring; a loop of fairly stout mild steel wire is passed over the first of these hooks, and the two ends, after traversing the stopper on either side of the sleeve, are sprung under the second, the elasticity of the wire keeping it securely in position.

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CIV.—*Influence of Water on the Boiling Point of Ethyl Alcohol at Pressures Above and Below the Atmospheric Pressure.*

By JOHN WADE, D.Sc., and RICHARD WILLIAM MERRIMAN, M.A.

ALTHOUGH it is half a century since Roscoe communicated to this Society the results of his now classical work on the composition of aqueous acids of constant boiling point (Roscoe and Dittmar, Trans., 1859, **12**, 128; Roscoe, *ibid.*, 1860, **13**, 146; 1862, **15**, 270),

the extensive field thus opened to investigators has remained practically untouched. Roscoe's isolation of mixtures of maximum boiling point was soon followed by the partial isolation of analogous mixtures of minimum boiling point by Wanklyn and Berthelot independently (*Proc. Roy. Soc.*, 1863, **12**, 334; *Ann. Chim. Phys.*, 1864, [iv], **1**, 384), and later by the complete isolation of a mixture of this class by Thorpe (*Trans.*, 1879, **35**, 544). But although the existence of a very large number of such physico-chemical individuals has since been established, no further attempt has been made to determine the variation in their composition when the pressure under which they are fractionated is changed.

The reason is probably to be found in the experimental difficulties involved. The isolation of mixtures of maximum boiling point can be effected without elaborate fractionation by Roscoe's simple expedient of distilling off any excess of either constituent until the composition of the less volatile residual mixture remains unchanged. But the composition of the more volatile fractions separated under such conditions is, as he found, variable and indeterminate, and although this is immaterial so long as it is the least volatile phase which is to be isolated, even approximately exact separation of the most volatile phase is, as Young has shown (*Trans.*, 1899, **75**, 679), impracticable without the aid of a very efficient fractionating column.

In the course of an investigation into the influence of water and alcohols on the boiling point of esters (Part I, Wade, *Trans.*, 1905, **87**, 1656), the present authors have accumulated results which have rendered desirable an extension of the work to pressures both above and below that of the atmosphere, and it is with this object that the apparatus described in the preceding communication has been devised. The results obtained incidentally with mixtures of ethyl alcohol and water have proved to be in some respects so different from what might legitimately have been anticipated, as to call for separate treatment.

I. *Formation of Azeotropic Mixtures of Ethyl Alcohol and Water under Pressures from 1450 mm. to 100 mm. of Mercury.*

The depression in the boiling point of ethyl alcohol produced by water under atmospheric pressure is relatively so slight (0.15°) that the curve expressing the relation of boiling point to composition is practically horizontal for a considerable distance on either side of the mixture of maximum volatility (Noyes and Warfel, *J. Amer. Chem. Soc.*, 1901, **23**, 463). Consequently it is not practicable, even with a very efficient fractionating column, to separate this mixture with any great exactness from spirit containing a

larger or smaller proportion of water. As, however, a mixture of maximum volatility necessarily behaves as a homogeneous mixture when distilled, the exact composition of the aqueous alcohol in question may be arrived at by Roscoe's method of approximation (*loc. cit.*); it was in this way that Young and Fortey (Trans., 1902, **81**, 719) established that under normal atmospheric pressure it boils at 78.15° , and contains 95.6 per cent. of alcohol. As there was no reason to anticipate any material increase in the depression of boiling point at pressures other than the atmospheric pressure, the present authors, in extending Young and Fortey's work, have adopted substantially their method, the only modification being the substitution of algebraical for graphical interpolation.

a. *Experimental Method.*

At each particular pressure, spirit which had been diluted to such concentration as seemed likely to furnish a homogeneous distillate, was fractionated with the precautions already detailed (this vol., pp. 989, 994). The densities of an early and a late fraction were then determined; if the density rose as the fractionation proceeded, the first fraction contained more water than the homogeneous mixture of constant boiling point; whilst if it fell, less water was present than in this mixture. By trial, two products were thus eventually obtained, which differed very little in density and composition, but were on opposite sides of the homogeneous mixture sought. The composition of the latter could then be calculated with sufficient exactness from the relative gradients of separation, obtained by dividing the respective density increments by the relative increase in the total amount distilled (see examples below).

The fractionations at 100 mm. and upwards were made through an 8-section, and those at lower pressures through a 12-section evaporator column. The boiling points were reduced to the hydrogen scale, and the pressures corrected to 0° and Lat. 45° . The manostat (this vol., p. 984) was in each case set approximately to the desired pressure, and when the accumulated observations allowed of the construction of a first differential curve (dt/dp), each set of temperatures was reduced to a uniform mean pressure. The densities were determined at 0° in pyknometers of Gay-Lussac type; they were corrected for buoyancy by the method previously described by the authors (Trans., 1909, **95**, 2180), and are accurate to ± 0.00001 , corresponding with 0.003 per cent. of water. For the calculation of the percentage of water a table was constructed from Mendeléeff's data (*Ann. Phys. Chem.*, 1863, **103**, 230) by the method of second differences. The variations in temperature were

so small that the calculation of the usual differentials of percentage weight against temperature would have been meaningless.

Excluding preliminary work, upwards of fifty fractionations were made under the various pressures. The results are given in summarised form in the following section. Their general character, as well as the method of reduction, will be gathered from the following detailed examples, which comprise the final pairs of fractionations under a high and a low pressure respectively.

(i) Pressure 1075 mm.; dt/dp 0.024° per mm.

a. Low Density: Alcohol, density 0.8201 (=water 4.62 per cent.), 155.0 grams.

Fraction.	a.	b.	c.	d.
Barometer	760.3	760.2	760.0	760.0
Manometer	311.9	311.7	312.6	312.4
Total pressure	1072.2	1071.9	1072.6	1072.4
B. p.	87.00°	87.01	87.01	87.03
,, reduced to 1075 mm.	87.07°	87.08	87.07	87.09
Weight of fraction	30.0	23.0	24.5	29.5
Stage of distillation*	0.10	0.27	0.40	0.60
Density at $0^\circ/4^\circ$	—	0.82014	—	0.82010
Percentage of water.....	—	4.630	—	4.618

Gradient of separation : $(4.618 - 4.630)/0.33 = -0.036$.

*Proportion of whole distillate which has passed over at the middle point of each fraction.

b. High Density: Alcohol, density 0.8206 (=water 4.79 per cent.), 162.0 grams.

Fraction.	a.	b.	c.	d.	e.
Barometer	766.9	767.2	767.2	767.2	767.2
Manometer.....	308.9	308.6	309.2	309.6	309.6
Total pressure	1075.8	1075.8	1076.4	1076.8	1076.8
B. p.	86.99°	87.02	87.05	87.05	87.05
,, reduced to 1075 mm....	86.97°	87.00	87.02	87.01	87.01
Weight of fraction	7.0	25.5	26.0	27.0	30.1
Stage of distillation	0.04	0.12	0.34	0.45	0.62
Density at $0^\circ/4^\circ$	—	0.82047	—	—	0.82056
Percentage of water	—	4.746	—	—	4.778

Gradient of separation : $(4.778 - 4.746)/0.50 = +0.064$.

Percentage of water in homogeneous mixture, $4.630 + \frac{0.036(4.746 - 4.630)}{0.036 + 0.064} = 4.67$.

Mean boiling point, 87.04° .

(ii) Pressure 200 mm.; $dt/dp = 0.103^\circ$ per mm.

a. Low Density: Alcohol, density 0.8142 (=water 2.61 per cent.),
172.4 grams.

Fraction.	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>	<i>f.</i>
Barometer.....	772.7	772.7	772.7	772.7	772.7	772.6
Manometer	574.2	574.4	574.9	574.1	574.0	573.9
Total pressure	198.5	198.3	197.8	198.6	198.6	198.7
B. p.	47.80°	47.73	47.69	47.85	47.82	47.83
„ reduced to 200 mm.	47.95°	47.91	47.92	47.99	47.96	47.97
Weight of fraction	11.6	25.4	23.4	24.0	22.5	25.5
Stage of distillation...	0.03	0.14	0.28	0.42	0.55	0.69
Density at 0°/4°	—	0.81428	—	—	—	0.81424
Percentage of water.....	—	2.626	—	—	—	2.612

Gradient of separation : $-0.014/0.55 = -0.025$.

b. High Density: Alcohol, density 0.8154 (=water 2.99 per cent.),
150.5 grams.

Fraction.	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>
Barometer.....	769.4	769.4	769.5	769.5	769.5
Manometer	571.1	571.2	571.2	571.5	571.9
Total pressure	198.3	198.2	198.3	198.0	197.6
B. p.	47.79°	47.78	47.79	47.73	47.70
„ reduced to 200 mm.	47.97°	47.97	47.97	47.94	47.95
Weight of fraction	13.5	25.1	26.0	25.0	26.5
Stage of distillation ...	0.09	0.17	0.34	0.51	0.68
Density at 0°/4°	—	0.81525	—	—	0.81537
Percentage of water.....	—	2.949	—	—	2.990

Gradient of separation : $+0.041/0.51 = +0.080$.

Percentage of water in homogeneous mixture : $2.626 + \frac{0.025(2.949 - 2.626)}{0.025 + 0.080} = 2.70$.

Mean boiling point, 47.95°.

b. General Results.

The following summary includes only the final observations under each pressure, the details being sufficiently illustrated by the foregoing examples. The series under 1450 mm. and 65 mm. pressure were the first to be examined; the comparatively large number of fractionations in each was due to the necessarily tentative character of the experiments, and the somewhat unexpected nature of the changes observed. The remaining series were investigated at a stage when the general trend of the composition-pressure curve having become evident, it was possible to anticipate the composition under any particular pressure with a fair approach to accuracy.

The depression of the boiling point below that of anhydrous alcohol at corresponding pressures is too small to warrant exact formulation; below 200 mm. it ceases to be measurable, largely, no doubt, because of the difficulty of comparison, due to the rapid change of temperature with pressure in this region. The fact, however, that at 130 mm., and probably at 100 mm., aqueous alcohol

passes over in advance of spirit containing less water, is sufficient evidence of its greater volatility, and confirms the already obvious fact that a very efficient still-head is a more sensitive thermoscope than a mercurial thermometer in its ordinary form.

In the early distillations under the lowest pressures, considerable trouble was occasioned by the absorption of atmospheric moisture during the various manipulations. By the time that the final fractionations were reached, however, these difficulties had been overcome. The high fractionation of the tenth set was made in order to test the efficiency of the apparatus in this respect. The alcohol used contained 0.138 per cent. of water, of which substance the 93.6 grams fractionated therefore contained 0.129 gram. The 41.8 grams of distillate contained 0.046 gram of water, and the 50.2 grams of residue, 0.076 gram, the "loss" (chiefly liquid adhering to the long column, etc.) being 1.6 gram. The water found after distillation was therefore 0.122 gram, or, including the "loss" in the residue, 0.124 gram, an amount experimentally identical with that originally present. There was, therefore, no accidental absorption of moisture at any stage.

TABLE I.—*Characteristic Data of Azeotropic Mixtures of Alcohol and Water.*

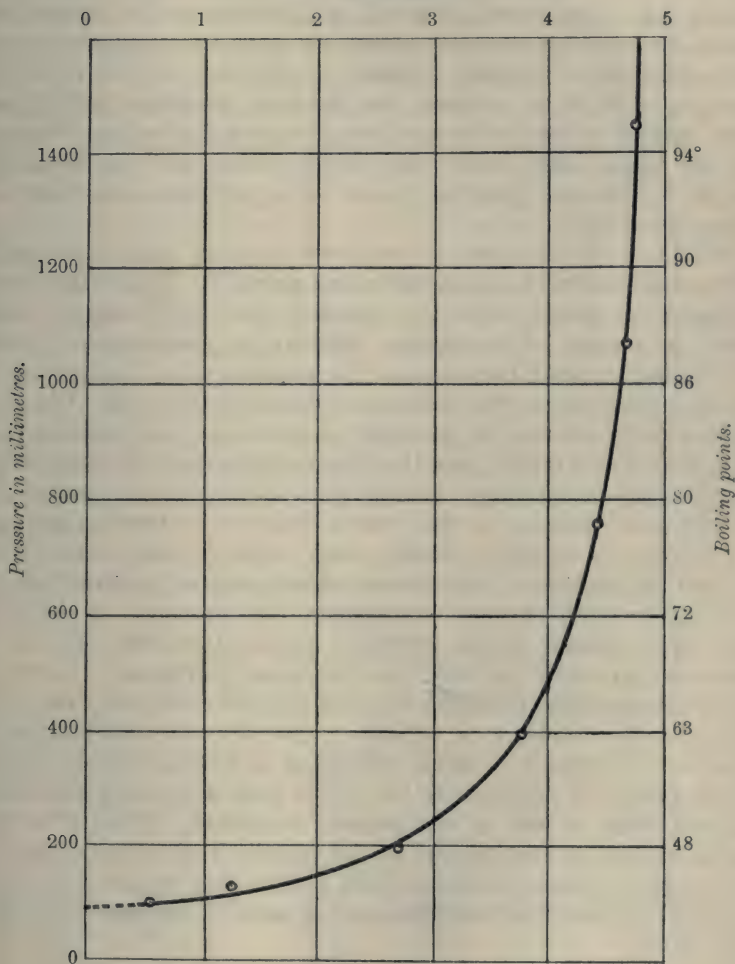
Results of fractionations.												
Pres- sure B p. of of in anhydrous series. mm. alcohol.			No. of frac- tions series.		Early fractions.		Late fractions.		Constants of binary mixture.			
			dp (per mm.)		Water, per cent.	Stage.	Water, per cent.	Stage.	Mean b.p.	Mean percentage water (c.)	$\frac{ds}{dp}$ (per mm.)	
1.	1450	95.5°	0.020°	11	{ 4.433 4.953	{ 0.08 0.12	{ 4.353 5.037	{ 0.47 0.46	{ 95.35° 95.36	4.73	0.0001	
2.	1075	87.26	0.024	2	{ 4.630 4.746	{ 0.27 0.12	{ 4.618 4.778	{ 0.60 0.62	{ 87.07 86.99	4.67	0.0004	
3.	760	78.39	0.033	3	{ 4.290 4.411	{ 0.14 0.20	{ 4.192 4.416	{ 0.62 0.80	{ 78.13 78.13	4.41*	0.0011	
4.	400	not detd.	0.058	1	3.770	0.20	3.776	0.69	62.85	3.77	0.0034	
5.	200	47.97	0.103	4	{ 2.626 2.949	{ 0.14 0.17	{ 2.612 2.990	{ 0.69 0.68	{ 47.95 47.96	2.70	0.0096	
6.	130	39.35	0.148	6	{ 1.143 1.330	{ 0.16 0.13	{ 1.127 1.344	{ 0.63 0.66	{ 39.29 39.39	1.25	0.025	
7.	100	34.2	0.180	1	0.537	0.15	0.537	0.64	34.2	0.54	0.036	
8.	75	29.35	0.232	4	0.071	0.12	0.083	0.69	—	—	no evidence of formation of homo- geneous product.	
9.	65	25.9	0.260	8	0.071	0.09	0.083	0.68	—	—		
10.	55	23.6	0.296	3	{ 0.019 0.035	{ 0.22 0.13	{ 0.151 0.041	{ 0.81 0.75	{ — —	—		

* Young and Fortey found b. p. 78.15° and 4.43 per cent. of water. The corresponding densities are 0.81950 (W. and M.) and 0.81941 (Y. and F.); Young and Fortey apparently used linear interpolation in calculating the composition from Mendeléeff's data; with differential interpolation a density of 0.81941 corresponds with 4.38 per cent. of water.

From these data, as embodied in the accompanying curve (Fig. 1),

in which composition is plotted against pressure, it is clear that under pressures of 100 mm. and upwards ethyl alcohol forms with water an infinite series of hylotropic mixtures of minimum boiling

FIG. 1.

Percentage of Water.*Azeotropic mixtures of ethyl alcohol and water.*

point. The proportion of water in these mixtures increases with the pressure, but although the rate of increase, which is at first very rapid, eventually becomes almost imperceptible, there is no evidence, so far as the present data serve, of a stage at which

further increase of pressure is unaccompanied by further change in composition; the curve appears to be asymptotic at its upper end, and bears a general resemblance to a rectangular hyperbola.

At pressures below 100 mm. there is not only no direct evidence of the formation of hylotropic mixtures, but much indirect evidence against it; in particular, the general trend of the curve leaves little doubt that, if produced, it would, as indicated by the broken line in the diagram, cut the zero ordinate at a pressure of about 80 mm. This question is further discussed at the end of the following section, in which it is shown that the clear resolution of 99.9 per cent. alcohol in the tenth series, and the comparative indefiniteness of the other results under very low pressures, are precisely what might be inferred from the results of a continuous fractionation there described.

While these mixtures of minimum boiling point resemble Roscoe's mixtures of maximum boiling point (*loc. cit.*) in that their composition changes with the pressure, they differ sharply from them in the sign of the change; whereas the percentage of water in aqueous alcohol increases as the pressure rises, the reverse is the case with the aqueous halogen acids and formic acid. Observations already obtained in the study of esters (*loc. cit.*) indicate that this difference is typical, and that it is probable that the composition of mixtures of minimum boiling point is in general changed by alteration of pressure in the reverse direction to that experienced by mixtures of maximum boiling point under the same conditions.

As the members of both classes of mixtures of constant boiling point share with chemical individuals the property of forming hylotropic gaseous phases (Ostwald, *Trans.*, 1904, **85**, 511), it is proposed, in order to avoid the cumbrous periphrase "mixtures having a minimum (or maximum) boiling point," to designate them as *azeotropic mixtures* (α , privative; ζέω. to boil). An azeotropic mixture resembles a chemical individual in boiling without undergoing change of composition, but differs from it in losing this fixed characteristic as soon as the pressure is altered. There is as yet no indication at any pressure of the transition of an azeotropic or temporarily hylotropic mixture into a more permanently hylotropic substance or chemical individual, as suggested by Ostwald and Wald (*loc. cit.*).

II. Continuous Fractionation of Aqueous Alcohol under Low Pressures.

It follows from the preceding results that unless the composition-pressure curve of aqueous alcohol is subject to some altogether abnormal inflection at pressures below 100 mm., anhydrous alcohol

constitutes the most volatile phase of aqueous spirit at any pressure below the point of intersection with the zero ordinate. It should therefore be possible to obtain anhydrous alcohol from ordinary spirit by systematic fractionation under low pressures; and even if this is not literally practicable, a very marked reduction in the amount of water may be confidently anticipated.

In order to test the correctness of this inference, commercial rectified spirit was subjected to a continuous series of fractionations through a 12-section evaporator column under 57—59 mm. pressure. It was not practicable with ordinary laboratory appliances to use the same specimen throughout the series; for even if half the spirit were distilled at each fractionation, the accumulation of the 25 grams required for the determination of the tenth density would necessitate the employment of 25×2^9 grams for the first fractionation—more than 16 litres.

At each stage, therefore, about 100 grams of spirit were distilled until about one-third had passed over; it was found that the exact proportion was immaterial, nearly half the spirit passing over under these conditions without any very marked increment of density. The density of the distillate having been determined, the next fractionation was effected with 100 grams of spirit as nearly as possible of identical composition, a correction being introduced for any slight discrepancy. In this way the following results were obtained:

TABLE II.—*Continuous Fractionation of Commercial Rectified Spirit.*

(i) *Experimental Results.*

Initial percentage of water, 5.14.

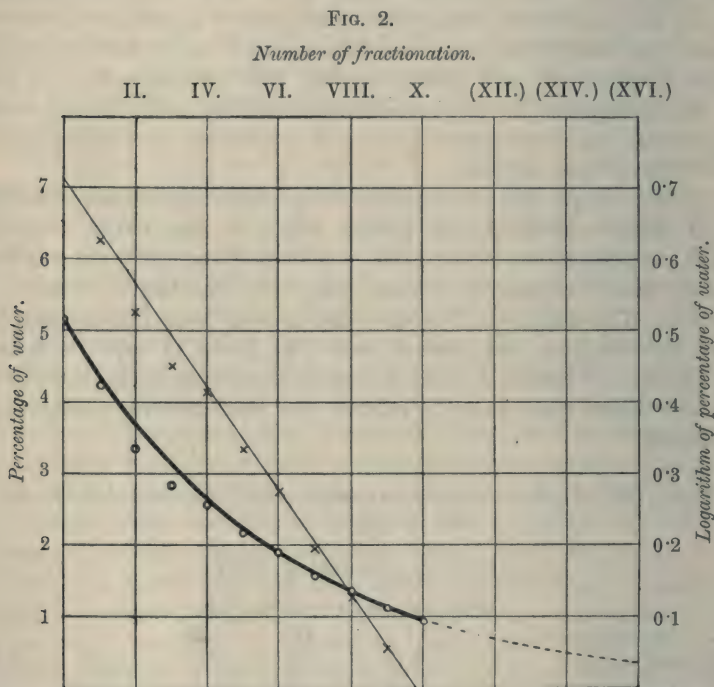
No. of fractionation	I.	II.	III.	IV.	V
Percentage of water	4.25	3.35	2.82	2.58	2.15
No. of fractionation	VI.	VII.	VIII.	IX.	X.
Percentage of water	1.90	1.57	1.33	1.14	0.95

(ii) *Extrapolated Values.*

No. of fractionation	XXI.	XXII.	XXIII.	XXIV.	XXV.
Percentage of water	0.148	0.125	0.106	0.089	0.075
No. of fractionation	XXVI.	XXVII.	XXVIII.	XXIX.	XXX.
Percentage of water	0.064	0.054	0.046	0.038	0.032
No. of fractionation	XXXI.	XXXII.	XXXIII.	XXXIV.	XXXV.
Percentage of water	0.027	0.023	0.020	0.017	0.014

Plotting these percentages against the number of fractionations (Fig. 2), it will be seen that, with the exception of the second and

third, they fall on a regular logarithmic curve, the corresponding logarithms ($\times 10$) falling, with the same exceptions, on a straight line. It follows that by a systematic fractionation under the above conditions the percentage of water is decreased in geometrical proportion to the number of fractionations. The results from the fourth fractionation onwards fall so evenly on the curve that further experiment was unnecessary, and extrapolation legitimate. The position of points on the extrapolated curve, a portion of



Systematic fractionation of aqueous alcohol under 57–59 mm. pressure.

which is indicated by the broken line in the diagram, may accordingly be calculated by means of the equation:

$$\log p = \log 5.14 - 0.0733n = 0.711 - 0.0733n,$$

where p is the percentage of water after the n th fractionation, and 0.0733 the logarithmic difference per fractionation.

Hence, by the end of the fourteenth fractionation the percentage of water should be reduced to 0.5; by the end of the nineteenth to 0.2; by the end of the twenty-third to 0.1; and by the end of the thirty-seventh to 0.01. Meanwhile the actual decrement at each fractionation should grow proportionally smaller. Between the

twenty-first and twenty-second fractionations it should be 0.023, namely, from 0.148 to 0.125 per cent.; in the high fractionation of the tenth series (p. 1002) the observed reduction was from 0.138 to 0.109 per cent. Between the twenty-fifth and twenty-sixth fractionations it should be half this, namely, from 0.075 to 0.064; in the indecisive fractionation of the ninth series (*loc. cit.*) the observed reduction was from 0.08 to 0.07 per cent. Between the twenty-ninth and thirtieth fractionations the decrement should be 0.006; in the low fractionation of the tenth series the observed reduction was from 0.041 to 0.035 per cent.

As the corresponding decrement in density is now reduced to 0.00002, no very great weight can be attached to differences so closely bordering on the limits of experimental error*; nevertheless, it is significant that in each of the indeterminate fractionations of the eighth, ninth, and tenth series the variation is in the required direction, and of the order required by the hypothesis laid down at the beginning of this section. It may be concluded that while there is no apparent limit to the elimination of water by fractionation under very low pressures, experimental verification much below 0.1 per cent. would necessitate the extension of pyknometrical accuracy to the sixth significant digit. It also follows that with modern large-scale rectifying apparatus there should be no difficulty in reducing the percentage of water in alcohol to a fraction of 1 per cent. by one or two rectifications under 50 mm. pressure.

III. *The Influence of Dry Air and of Moist Air on the Concentration of Alcohol.*

One of the most interesting observations of Roscoe and Dittmar in the course of their study of hydrochloric acid (*loc. cit.*) was that of the identity of the residue which remains after acid of any concentration has been evaporated in a current of air at a given temperature, with that which remains when the same acid is fractionated under the pressure corresponding with that temperature. The assumption of a limiting pressure below which alcohol and water cease to form an azeotropic mixture necessitates a similar corollary, namely, that at temperatures below that corresponding with the limiting pressure, anhydrous alcohol, even under ordinary atmospheric pressure, should be the most volatile phase present in aqueous spirit.

From the data already given, the temperature of saturated alcohol

With proper correction for buoyancy (*loc. cit.*), however, it is very rarely that duplicate densities of a moderately volatile liquid such as alcohol differ by more than 0.00001; when, in exceptional cases, the difference has exceeded 0.00002, investigation has usually afforded an explanation of the discrepancy.

vapour under 55 mm. pressure is 23.7° , which, considering the rapidity with which the boiling point changes with pressure in this region, agrees fairly well with Richardson's value of $23.1^{\circ}/54.9$ mm. (Trans., 1886, **49**, 762) obtained by a statical method. Hence if moist alcohol be evaporated at ordinary atmospheric temperatures, the evaporated portion should contain less, and the residue more water than the original spirit. In these circumstances the passage of a current of air should be equivalent to a systematic fractionation through an efficient still-head.

(a) *Dry Air.*

On testing this conclusion experimentally it was again found to be entirely borne out by the facts. Spirit of four different strengths was allowed to evaporate for an extended period into air of identical dryness. For this purpose quantities of about 200 grams were placed in four filtering flasks, through a caoutchouc stopper in the neck of each of which a gas delivery tube passed to the bottom of the liquid. The side-tubes of the flasks were connected through regulating taps with vessels in which a vacuum was maintained, a drying tower being interposed to eliminate any risk of backward diffusion of moisture from the pump. The four gas delivery tubes were connected with a large drying apparatus, in which air, filtered through cotton-wool, was first drawn in succession through two large towers, each containing about 3.5 kilograms of porous calcium chloride, and then, after a second precautionary filtration, through two wash-bottles of sulphuric acid. Ordinary drying apparatus was found to be inadequate.

After each twenty-four hours from the start the flasks were temporarily disconnected, and weighed, and samples poured through the side-tube directly into the pycnometer fillers. The main experiment was stopped at the end of the second day, but subsidiary experiments were continued for three and four days respectively. The rate of evaporation was variable, largely by reason of the difficulty in maintaining an exact rate for the air current, although in some cases intentionally; the precise time occupied is of little significance, however, the rate of evaporation being proportional to the air supply. In order to facilitate comparison, the progressive diminution in weight is in each case expressed as a percentage of the original amount. The experiment was conducted in an unheated room at ordinary winter temperature, which remained constant between 9° and 10° . The results are given in the following table. The first four columns are self-explanatory; the fifth column gives the actual loss of water (that is to say, the amount carried off by

the spirit evaporated); the sixth, the loss which would have been possible if the spirit had evaporated as a whole; the seventh, the ratio of actual to possible loss, or, in other words, the degree of fractionation. The percentages are, as before, correct to ± 0.003 .

TABLE III.—*Fractionation of Aqueous Alcohol by Evaporation in Dry Air.*

Days.	Relative weight of spirit.	Density at 0°/4°.	Water in spirit.		Total loss of water.		
			Percentage.	Grams.	Observed.	Calculated for homogeneous evaporation.	Ratio of actual to possible loss.
0	100.00	0.80631	0.020	0.020	—	—	—
1	86.66	0.80633	0.026	0.022	(-0.002)	0.003	—
2	82.28	0.80632	0.023	0.019	0.001	0.004	—
0	100.00	0.80798	0.556	0.556	—	—	—
1	95.02	0.80800	0.562	0.534	0.022	0.028	—
2	90.46	0.80799	0.559	0.506	0.050	0.053	—
0	100.00	0.80782	0.505	0.505	—	—	—
4	50.80	0.80813	0.604	0.303	0.202	0.273	0.74
0	100.00	0.81054	1.386	1.386	—	—	—
3	36.8	0.81150	1.701	0.626	0.760	0.986	0.77
0	100.00	0.81304	2.210	2.210	—	—	—
1	95.03	0.81313	2.241	2.130	0.080	0.111	0.72
2	87.76	0.81317	2.254	1.978	0.232	0.272	0.85
0	100.00	0.82301	5.645	5.645	—	—	—
1	92.75	0.82325	5.730	5.289	0.356	0.412	0.87
2	82.54	0.82358	5.847	4.827	0.818	1.003	0.81

The first set, with practically anhydrous alcohol, shows that the moisture in the air had been reduced to a negligible quantity, at the most 5 mg. in the two days. The second set, with 99.5 per cent. spirit, was indecisive, the density increments only just exceeding the possible experimental error. As this might have been due to the relatively small amount evaporated, the experiment was repeated until about half the spirit had been volatilised; the fractionation was now unmistakable, and of the same order as in the remaining series. The third set, with 98 per cent. spirit, shows a clear separation, especially at the end of the first day; at the end of the second day differentiation had not increased in the same proportion, although it was still proceeding. A supplementary experiment with somewhat stronger spirit, extending over three days, during which nearly two-thirds of the liquid was evaporated, confirmed these results, showing an intermediate degree of fractionation. The fourth set, made with ordinary rectified spirit, does not require comment.

It is clear that spirit containing an appreciable amount of water becomes weaker when exposed to dry air, owing to the more rapid evaporation of the alcohol. The inability of alcohol to form stable mixtures with water at pressures and temperatures below a certain limit thus receives additional confirmation.

(b) *Moist Air.*

The trouble caused by the access of moist air to the alcohol during the preliminary fractionations under low pressure and the corresponding density determinations, seemed to support the common belief that alcohol is a hygroscopic substance. The preceding results, however, suggested the possibility of another explanation, namely, the preferential evaporation of the stronger spirit; it was therefore desirable to submit the question to an experimental test. Open flasks containing about 100 grams of spirit, which only partly filled them, were placed under a large bell-jar in a pan containing enough water to form an effective seal, and there left in an unheated room in winter; the mouths of the flasks were protected by loose caps of filter paper from possible contamination with condensed liquid. The densities were determined on three successive days, with the results shown in the following table. Although, as will be noticed, the spirit in each case increased in density, the contents of the flasks did not gain in weight, but, on the contrary, lost a small amount.

TABLE IV.—*Influence of Moist Air on the Density of Alcohol.*

Days.	Density at 0°/4°.	Water per 100 grams.		Total loss of weight observed.	Net loss of weight = alcohol.	Ratio of gain of water to loss of alcohol.
		Weight.	Gain.			
0	0·80656	0·14	—	—	—	—
1	0·80664	0·16	0·02	not determined	—	—
2	0·80674	0·22	0·08	„ „	—	—
0	0·80757	0·46	—	—	—	—
1	0·80768	0·50	0·04	not determined	—	—
2	0·80786	0·56	0·10	„ „	—	—
0	0·81054	1·39	—	—	—	—
1	0·81073	1·45	0·07	0·10	0·17	0·4
2	0·81091	1·51	0·12	0·29	0·31	0·4
0	0·82342	5·79	—	—	—	—
1	0·82355	5·84	0·05	0·11	0·16	0·3
2	0·82368	5·88	0·09	0·25	0·34	0·3

At first sight it seems rather significant that the increments of density in the above series are of the same order as those observed

in the parallel experiments with dry air. The absence of any substantial amount of evaporation, however, negatives the possibility of fractionation, as the absence of any substantial gain in water equally negatives the possibility of hygroscopic absorption. Another explanation must therefore be sought. A volatile liquid, when exposed to a limited volume of air, must necessarily evaporate until equilibrium is reached; hence, not only will alcohol evaporate from the flasks, but water will also evaporate from the pan until the mixed vapours are in equilibrium with both. As the equilibrium is between all three phases, water vapour passes into the alcohol, and alcohol vapour into the water, until the respective vapour pressures are permanently balanced. And both the pressure and the density of alcohol vapour being greater than those of water at any particular temperature, the loss of alcohol should predominate markedly over the gain of water, as it does.

It must therefore be concluded that alcohol is not hygroscopic in the ordinary sense. Nevertheless, the elimination of small quantities of water from nearly anhydrous spirit is, as the experiments in the earlier part of this communication have shown, so slow and partial a process, even under the most favourable conditions, that if dry alcohol be agitated with moist air, the moisture which is washed out of the air, as any other vapour might be, is detained permanently in the spirit. Hence the need for elaborate precautions against atmospheric contact when working with anhydrous alcohol. Probably the origin of the very general belief in the specifically hygroscopic character of alcohol is to be found in the fact that absolute alcohol cannot be prepared from aqueous spirit by any ordinary process of fractionation. Now that it has been shown that this limitation ceases at low pressures, the belief has no longer any foundation.

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CV.—*Influence of Minute Quantities of Ferric Salts and of Manganese Nitrate on the Rate of Solution of Mercury in Nitric Acid.*

By PRAFULLA CHANDRA RÂY.

IN the course of my investigations on mercurous nitrite and its numerous derivatives, extending over the last fifteen years, it has often been necessary to prepare this substance in quantity. I have sometimes been struck with the remarkable fact that under analogous conditions the yield of mercurous nitrite has been very poor. This abnormal behaviour of nitric acid in isolated cases led me to undertake a close and systematic investigation of the disturbing causes. It was soon discovered that the retarding effect was due to the presence of minute quantities of iron in the acid; for, whenever the acid was redistilled in glass retorts, no such anomaly was noticed. As might be expected in these suspected cases, the residue, after the acid had been distilled, was invariably found to consist of ferric iron. Now Millon (*Compt. rend.*, 1842, 14, 904) and Veley (*Phil. Trans.*, 1891, A, 182, 279) have pointed out that the presence of ferrous sulphate, "which removes the nitrous acid as fast as it might be formed," serves to prevent the chemical change between nitric acid and the metals. The rôle played by ferric salts in retarding the chemical reaction has not, so far as I am aware, been studied. It was, therefore, thought desirable to investigate in a systematic manner the material deterioration in the solvent power of nitric acid when it is contaminated by the above salts, even in minute quantities. Incidentally, the effect of adding small quantities of manganese, and in some instances of sodium and potassium nitrates, was also studied.*

EXPERIMENTAL.

As a rule, three beakers of about 55 c.c. capacity were placed side by side on a flat and smooth tile, and 50 c.c. of dilute nitric acid, containing 10 c.c. of acid of $D_{30}^{20} 1.383$ and 40 c.c. of distilled water, were used. To the acid was added 1 to 2 c.c. of solutions of ferric, potassium, sodium, and manganese nitrates respectively, of known strengths. Mercury was then poured in. The mercury used

* While the present investigation was in progress, Rennie, Higgin, and Cooke's communication, "the interaction of copper and nitric acid in presence of metallic nitrates," appeared (*Trans.*, 1908, 93, 1162), and hence sodium and potassium nitrates were included.

for these experiments was first purified by the ordinary methods, and then distilled in a vacuum. In each experiment the weight of mercury used was 10 grams (within 0.003 gram).

One beaker was always set apart for a blank parallel experiment. Other details are given below, under the individual series of experiments. After the experiments were finished, the mercury was poured off, carefully washed free from the adhering impurities, and then dried in the usual manner, and weighed. The loss in weight was taken to represent the amount of mercury dissolved. As a rule, the reaction was allowed to proceed for two to two and a-half hours, and was stopped when minute crystals of mercurous nitrite had just begun to appear. The temperatures recorded are those of the laboratory between 11 a.m. and 3 p.m. during the months of September and October (1908), and it was during this interval of four hours that the experiments were performed. Only the initial temperatures are given. As each series of parallel experiments was carried on under exactly the same variations of temperature (generally within 1°), no thermostatic arrangement was made.

SERIES I.

	Blank.	Mn(NO ₃) ₂ . 2 c.c. sol.	KNO ₃ . 1 c.c. sol.	Duration of expt., minutes.	Temp.
Mercury consumed	1.76	1.83	1.89	160	30.4°
Ratio of nitric to nitric nitrogen in 1 c.c. of the bottom liquid.*	2.71	3.18	3.2	—	—
Sp. gr. of the bottom liquid	1.496	1.511	7.517	—	—

* Compare Trans., 1905, 87, 172.

1 c.c. Mn(NO₃)₂ gave 0.081 Mn₃O₄ (=19 per cent. solution) and 1 c.c. KNO₃ gave 0.0283 K₂SO₄ (=3.28 per cent. solution).

SERIES II.

	Blank.	Fe(NO ₃) ₃ . 1 c.c. sol.	NaNO ₃ . 1 c.c. sol.	Duration, of expt., minutes.	Temp.
Mercury consumed	1.55	1.38	1.81	120	30.4°

1 c.c. Fe(NO₃)₃ gave 0.0085 Fe₂O₃=0.00595 Fe (=2.57 per cent. solution).

1 c.c. NaNO₃ gave 0.055 Na₂SO₄ (=6.59 per cent. solution).

In this series of experiments, the position of the beakers on the tile remained unchanged, but sodium nitrate was substituted for potassium nitrate and ferric nitrate for manganese nitrate.

SERIES III.

	Blank.	Fe(NO ₃) ₃ . 1 c.c. sol.	NaNO ₃ . 1 c.c. sol.	Duration of expt., minutes.	Temp.
Mercury consumed	1.54	1.331	1.705	130	not recorded

In this series the conditions of the experiment were almost the same as in series II, only the beakers containing ferric nitrate and sodium nitrate were interchanged, and their positions as marked on the tile reversed.

SERIES IV.

	Blank.	NaNO ₃ . 1 c.c. sol.	Fe(NO ₃) ₃ . 1 c.c. sol.	Duration of expt., minutes.	Temp.
Mercury consumed.....	1.931	1.945	1.245	135	31°
Ratio of nitric to nitric } nitrogen in 1 c.c. of the } bottom liquid. }	3.22	3.20	3.5	—	—
Sp. gr. of the bottom liquid...	1.530	1.532	1.398	—	—

SERIES V.

	Blank.	Mn(NO ₃) ₂ . 2 c.c. sol.	Duration of expt., minutes.	Temp.
Mercury consumed.....	1.995	2.015	170	29.5°

SERIES VI.

*Retardation Caused by Ferric Sulphate.**

In this series, the beaker used in the blank experiment and that containing manganese nitrate, used in series V, were interchanged, and three parallel experiments were simultaneously started.

	Blank.	Mn(NO ₃) ₂ . 2 c.c. sol.	Fe ₂ (SO ₄) ₃ . 1 c.c. sol.	Duration of expt., minutes.	Temp.
Mercury consumed	1.848	2.260	1.583	145	29.4°

1 c.c. Fe₂(SO₄)₃ gave 0.001 Fe₂O₃ (=0.25 per cent. solution).

SERIES VII.

	Blank.	Fe ₂ (SO ₄) ₃ . 1 c.c. sol.	Duration of expt., minutes.	Temp.
Mercury consumed	1.890	1.781	155	29.5°

* Only very dilute solutions of ferric sulphate were used, as otherwise a precipitate of mercurous sulphate was formed, which served as a protective layer on the surface of mercury and interfered with the dissolution of the metal.

SERIES VIII.

The beaker used in the blank experiment and that containing ferric sulphate were interchanged.

	Blank.	$\text{Fe}_2(\text{SO}_4)_3$, 2 c.c. sol.	Duration of expt., minutes.	Temp.
Mercury consumed	1.775	1.602	145	28.4°

SERIES IX.

	Blank.	$\text{Fe}_2(\text{SO}_4)_3$, 2 c.c. sol.	Duration of expt., minutes.	Temp.
Mercury consumed	1.578	1.349	120	28.8

Discussion of Results.

It will be seen at a glance through the above series of experiments that ferric iron, even in minute quantities, distinctly retards the solvent action of nitric acid on mercury. The ferric salt was found to be free from even traces of ferrous iron. Ferric sulphate also behaved exactly like ferric nitrate; the former had to be used in much more dilute solutions, as otherwise mercurous sulphate was precipitated, which acted as a protective coating. For similar reasons, ferric chloride was objectionable. It would thus appear that the acid radicle, in this particular instance, plays no part. The explanation seems to lie in the alternate reduction and oxidation of the iron radicle—the triferrion being converted into diferrion, and vice versa. It is well known that nitrous acid behaves both as a reducing and oxidising agent. On this hypothesis, the atoms of triferrion simply act as catalysts. Manganese nitrate, and even sodium nitrate, have been found to act as accelerators, the former having the greater effect. Many experiments were also made with the sulphates of manganese, potassium, and sodium, using very dilute solutions for reasons explained above, and the conclusions to which these experiments lead are that these substances neither accelerate nor retard the action of nitric acid.

In the light of the present investigation, the view hitherto accepted as regards the part played by ferrous sulphate in destroying nitrous acid, and thus retarding the dissolution of a metal in nitric acid, has to be modified. Both ferrous and ferric sulphates are effective in this respect, the former, no doubt, to a larger extent. That the formation of nitrous acid is considerably retarded by ferric nitrate, is proved also by direct evidence. Thus, in series IV, the ratio of nitric to nitrous nitrogen in the bottom liquid is 3.22, 3.20, and 3.5 respectively. Moreover, the evolution of gases in the beaker containing the iron solutions was invariably slow.

How manganese and sodium nitrates act as accelerators is not easily explained. The discussion which took place on the occasion of the reading of Rennie, Higgin, and Cooke's paper (Proc., 1908, **24**, 141) does not throw much light on the subject, and apparently the question must be regarded as an open one.

It has been found that the amount of mercury dissolved in a given time, other conditions being the same, depends on the shape of the bottom of the beaker. In short, the more thinly the mercury is spread out, the less is the quantity of it that is dissolved, and vice versa. Paradoxical as the result might appear, the explanation is not far to seek. When the mercury is thinly spread out, the products of reaction are distributed over a larger area, whereas when the mercury is less elongated, the products of reaction become more concentrated in the neighbourhood of the metal, and this is precisely the condition favourable for more rapid dissolution of mercury (Veley, *loc. cit.*, p. 300). By the interchange of beakers, the errors due to what may be termed the idiosyncracies of the bottom were eliminated.

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CALCUTTA.

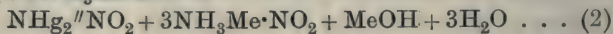
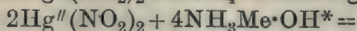
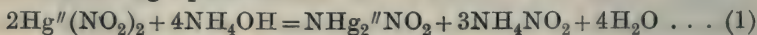
CVI.—*Methylammonium Nitrite.*

By PRAFULLA CHANDRA RÂY and JITENDRA NATH RAKSHIT.

THE preparation of dimercurammonium nitrite, $\text{NHg}_2''\text{NO}_2$, by the interaction of mercuric nitrite and aqueous ammonia has already been described by one of us (Trans., 1902, **81**, 644).

We have now treated a solution of mercuric nitrite with methylamine with a view to ascertain if the formation of a corresponding alkyl derivative takes place. The gelatinous, heavy precipitate, which was the result of the reaction, after being dried in the usual manner, was found, on analysis, to be dimercurammonium nitrite (Found, $\text{NHg}_2\text{NO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$: Hg=84.82; N=5.46. Calc., 85.29 and 5.97 respectively).

It now became almost evident that the two distinct reactions, both giving rise to dimercurammonium nitrite, take place according to the following equations:



* It is scarcely necessary to point out that the amine exists in solution as methylammonium hydroxide.

As it was feared that the methylammonium nitrite, if at all formed, could not be recovered by evaporation, as it would be decomposed at the temperature of boiling water, the filtrate, sometimes amounting to as much as 100 c.c., was subjected to distillation in a vacuum (compare Trans., 1909, **95**, 345). At a temperature of 45—50° nearly the whole of the water passed off, with occasional evolution of a gas, which proved to be pure nitrogen. The pale yellow residual liquid, amounting to not more than 4 or 5 c.c., had the consistency of a viscid syrup, and it did not further diminish in bulk or appreciably decompose, even when kept at the above temperature for a considerable time. The temperature was then gradually raised to 60°, which was maintained for two hours or more. A part of the substance began slowly to decompose, but at the end of this operation, on removal of the beaker of warm water in which the bulb was immersed, the viscid liquid solidified *en masse* in the shape of minute crystals. As the salt is extremely deliquescent, care should be taken to keep the upper part of the tube dry by enclosing it in a steam jacket, as otherwise the minute drops of water condensed inside the walls would be absorbed by it, crystallisation being thus retarded.

The process detailed above was a very tedious one, involving twelve to eighteen hours' heating, extending over two to three days. The syrupy liquid also behaved like a supersaturated liquid, and it was often not an easy task to hit off the exact moment of crystallisation. Moreover, as the precipitation of mercuric nitrite by ammonia and methylamine leaves distinct traces of mercury in the filtrate, the methylammonium nitrite obtained by the above method was somewhat impure. The crystalline deposit, when heated to 70° and upwards, decomposed, yielding methyl alcohol and nitrogen; and it also liberated iodine from a solution of potassium iodide acidified with dilute sulphuric acid. The possibility of the existence of this interesting compound being thus fully established, we set about its preparation according to the method described below.

Second Method of Preparation.—Pure methylamine hydrochloride was triturated in a mortar with silver nitrite, water being added from time to time. The end point of the reaction being carefully attained, the clear filtered solution was evaporated in a vacuum over sulphuric acid. In this manner lustrous crystals were obtained.

Analysis.—Great difficulty was experienced in the combustion analysis of the salt owing to its unstable character. Even when slowly and cautiously heated in a current of oxygen, it suddenly decomposed with a slight explosion and a flash of light, the latter due, probably, to the combustion of the liberated methyl alcohol,

and in such cases the potash bulb was at once filled with nitrous fumes. After several failures, the following method was adopted: the porcelain boat containing the substance was placed in the combustion tube screened off from the heated portion; in fact, every precaution was taken so that the temperature in this part did not exceed that of the surrounding atmosphere. A current of air was substituted for oxygen. Heated asbestos board was then held over the substance at a carefully regulated distance, in order that the temperature might not exceed 60° . The salt slowly decomposed with intumescence, and no further trouble took place. Finally, when there was no residue in the boat, and only minute drops of a resinous liquid were deposited on the combustion tube, the latter was raised to the temperature of red heat:

0.3035 gave 0.1751 CO_2 and 0.2052 H_2O . $\text{C}=15.73$; $\text{H}=7.51$.

0.0550 „ 17.3 c.c. N_2 at 24° and 760 mm. $\text{N}=35.45$.

$\text{CH}_6\text{O}_2\text{N}_2$ requires $\text{C}=15.1$; $\text{H}=7.70$; $\text{N}=35.95$ per cent.

The nitrogen was also estimated by the Crum-Frankland and the "urea" methods, and in both cases the percentage amounted to 17.97; in other words, only the nitritic nitrogen is set free.

A cryoscopic determination of the salt at a dilution of 13.5 litres gave the percentage of ionisation as 87, and at a dilution of 20 litres as 91. This shows that the degree of ionisation of this salt is of the same order as that of ammonium nitrite, tetramethylammonium nitrite, and the alkaline nitrites (compare Proc., 1910, 26, 173).

Properties.—The salt has a pale greenish-yellow tint, and is extremely deliquescent. When kept in a desiccator, it constantly loses in weight, the odour of methylamine being distinctly perceptible, and in a vacuum desiccator the loss is much greater, but it cannot be sublimed unchanged in a vacuum, as in the case of ammonium nitrite. When heated, it decomposes mainly into methyl alcohol and nitrogen, but secondary products are also formed. Methyl alcohol was detected in the distillate by oxidising the substance in the usual manner with potassium dichromate and sulphuric acid.

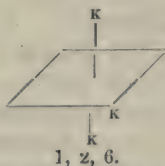
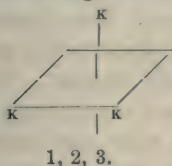
The action of heat on methylammonium nitrite is now being studied, and the preparation of some of its homologues is in progress.

CVII.—*The Isomerism of Ferrocyanides.*

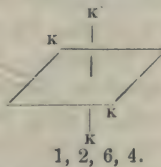
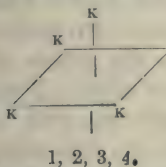
By SAMUEL HENRY CLIFFORD BRIGGS, D.Sc.

It was shown by Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413) that potassium ferricyanide exists in two forms, namely, the ordinary red or α -ferricyanide, and an olive-green salt or β -ferricyanide, which gives a reddish-violet solution, and was obtained by the action of acids on the ordinary modification. These authors thought that the two salts might possibly be stereoisomerides; but they drew no definite conclusion with regard to this relationship, since, according to Werner's theory of complex salts, ferricyanides should exist in only one form.

In a paper on the constitution of co-ordinated compounds, I described an alternative theory (*Trans.*, 1908, **93**, 1564), according to which potassium ferricyanide should exist in two stereoisomerides having the following formulæ:



If this theory is correct, ferrocyanides should also exist in two stereoisomerides, namely, 1, 2, 3, 4, and 1, 2, 6, 4, using Werner's notation for the different corners of the octahedron:



It was observed that large-scale preparations of potassium ferrocyanide, as seen at the Franco-British Exhibition in 1908, varied in colour from lemon-yellow to amber-yellow, and that sodium ferrocyanide was usually quite distinct in colour from potassium ferrocyanide, although the two compounds are alkali salts of the same acid.

It was thought that these differences in colour might be due to the existence of two classes of ferrocyanides, in agreement with the above formulæ, and the investigation described below was therefore undertaken.

The work has shown that ferrocyanides exist in two modifications which are related to each other in precisely the same way as the

α - and β -ferricyanides of Locke and Edwards, and which will therefore be called α - and β -ferrocyanides. The two forms differ in colour. They also exhibit slight differences in density and solubility, and are probably stereoisomerides.

The first part of the paper contains an account of the preparation of eight ferrocyanides in the two modifications. In the second part, the relationship of the two forms is discussed.

PART I.

Potassium Ferrocyanides, $K_4Fe(CN)_6 \cdot 3H_2O$.

Potassium ferrocyanide has been investigated more particularly by Bunsen (*Pogg. Ann.*, 1835, **36**, 404), Wyruboff (*Ann. Chim. Phys.*, 1869, [iv], **16**, 293), and Dufet (*Compt. rend.*, 1895, **120**, 377); but none of these chemists appears to have given much attention to the colour of the salt. In Dammer's *Handbuch* (Vol. III, p. 368) it is described as "zitronen- bis orangegelben . . . Kryst. (Bunsen)." In Roscoe and Schorlemmer's treatise (1895 edition, Vol. II, Part II, p. 107) the crystals are said to be "of a lemon-yellow colour, and generally opaque. Small crystals, on the other hand, are amber-coloured and transparent." As shown below, this statement is scarcely correct, since the lemon-yellow and amber-yellow crystals represent the α - and β -forms respectively, independently of the size of the crystals.

Preparation of Potassium β -Ferrocyanide.—Locke and Edwards (*loc. cit.*) prepared potassium β -ferricyanide by the action of acids on the ordinary form. In order, therefore, to prepare a second modification of potassium ferrocyanide, the action of acids on Kahlbaum's potassium ferrocyanide was studied. Two difficulties were encountered, arising from the readiness with which acid solutions of ferrocyanides oxidise in the air, becoming blue, and from the ease with which a white decomposition product is precipitated on heating. It was therefore necessary to use a minimum quantity of acid, and to work in the absence of air and at as low a temperature as possible.

(1) A solution of 60 grams of potassium ferrocyanide in 130 c.c. of water at 50° was poured into a flask, and the air above the liquid was displaced by carbon dioxide. One c.c. of glacial acetic acid diluted with 3 or 4 c.c. of water was added from a dropping funnel, and the solution allowed to cool slowly, the flask being tightly corked. The crystals which separated after some time had a bright amber colour, as distinguished from the lemon-yellow of Kahlbaum's potassium ferrocyanide. These crystals contained a

trace of the white decomposition product, in consequence of which they became green on exposure to light. The preparation was therefore modified, a cold solution of potassium ferrocyanide being used as follows.

(2) Twenty-five grams of potassium ferrocyanide were dissolved in 100 c.c. of water, and the cold solution was treated with 2.5 c.c. of diluted acetic acid (1 vol. glacial acetic acid diluted to 10 vols. with water). The liquid was then poured into a flask, which it completely filled, no air space remaining, and the flask was tightly stoppered. After twenty-four hours the solution was filtered and mixed with alcohol, and the pure potassium β -ferrocyanide was obtained as a cream-coloured, crystalline precipitate. This was collected, washed with alcohol until free from traces of acid, and dried with ether.

Preparation of Potassium α -Ferrocyanide.—The white decomposition product obtained by the action of acids is probably potassium ferrous ferrocyanide or ferrous cyanide, resulting from a slight dissociation of the salt into simple cyanides (compare Berthelot, *Ann. Chim. Phys.*, 1900, [vii], 21, 204). It was thought that the addition of potassium cyanide as well as acid in the preparation of potassium β -ferrocyanide might prevent this decomposition by reducing the tendency to dissociate into simple cyanides. This proved to be the case, and no white precipitate separated, but the crystals obtained from a solution containing potassium cyanide as well as acid were lemon-yellow, and paler in colour than Kahlbaum's salt. A clue was thus obtained to the preparation of potassium α -ferrocyanide. Twenty-five grams of potassium ferrocyanide (Kahlbaum) and 0.25 gram of potassium cyanide were dissolved in 100 c.c. of water, and the solution was allowed to remain for a day. Alcohol was then added, and potassium α -ferrocyanide was obtained as a pure white, crystalline precipitate, which was collected, washed well with alcohol, and dried with ether.

Analysis.—Eight preparations were analysed: (1) was Kahlbaum's salt (chiefly α -ferrocyanide), recrystallised once from water; (2) was a slightly paler specimen (α -ferrocyanide), obtained by recrystallising Kahlbaum's salt from a solution containing potassium hydroxide (see p. 1025); (3) was potassium α -ferrocyanide, prepared from a solution containing potassium cyanide; (4), (5), (6), (7), (8) were potassium β -ferrocyanide, obtained from Kahlbaum's salt by the action of acetic (4 and 5), hydrochloric, sulphuric, and nitric acids respectively, in the manner already described.

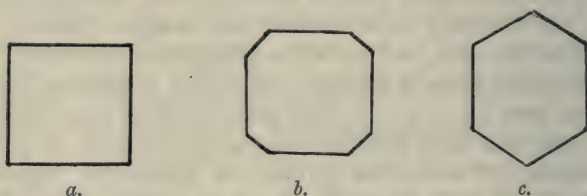
Nitrogen was determined by decomposing the salt with concentrated sulphuric acid, and estimating the ammonia produced in the usual way.

Iron was determined by titration with *N*/10-permanganate, and water by dehydration in the steam-oven.

No.	(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	Required for $K_4Fe(CN)_6 \cdot 3H_2O$.
N ...	19.96	19.98	20.2	19.86	19.87	—	—	—	19.90
Fe ...	13.29	13.27	13.29	13.22	13.25	13.28	13.24	13.28	13.22
H ₂ O	12.73	12.66	12.66	12.98	12.82	—	—	—	12.80

It is evident from these results that the deeper colour of the β -modification is not caused by the presence of an impurity which can be detected by quantitative analysis. It might, however, be due to a trace of very highly coloured impurity, too small in amount to affect the analysis. This possibility is discussed and disproved below (p. 1033).

Crystalline Form.—No crystallographic examination has been made. As the salts crystallise together in all proportions, and are generally so very similar in properties, marked crystallographic differences are not to be expected. There is, however, a distinct difference in the appearance of the crystals; possibly a difference in habit. Potassium ferrocyanide separates from solution in thin plates of various shapes. The most usual are shown diagrammatically in Fig. 1.



When a solution of potassium β -ferrocyanide is slowly evaporated over sulphuric acid, the square plates shown in *a* are generally produced, the four corners of which are clearly defined. From a solution of α -ferrocyanide the plates have the shape given in *b*. With a mixture of the two, the shorter edges of the irregular octagon are not so strongly marked, the appearance approaching more to *a*. The six-sided plates marked *c* are obtained from solutions of each form, but usually from the α -ferrocyanide.

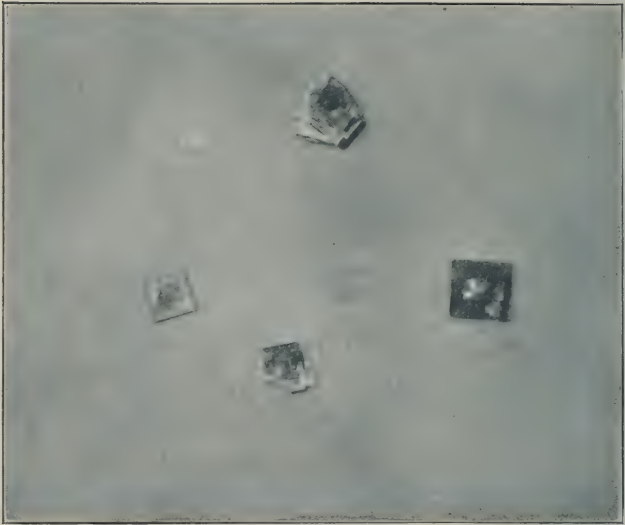
Fig. 2 shows crystals of the β -ferrocyanide obtained by slow evaporation over sulphuric acid. Fig. 3, for which I am indebted to Mr. Howard Priestman, is a photo-micrograph of crystals obtained by spontaneous evaporation of a solution of the α -ferrocyanide on a microscope slide. The crystals are mostly the six-sided plates marked *c* in Fig. 1.

A remarkable difference in the capillary properties of the crystals of the two ferrocyanides was observed. When a concentrated

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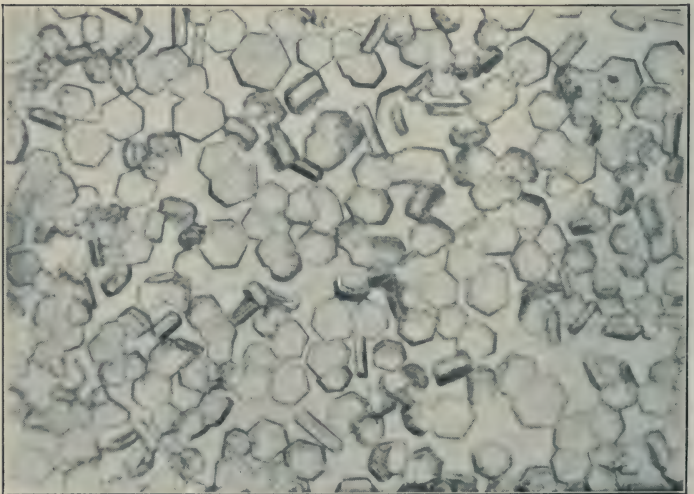
FIG. 2.



Potassium β -ferrocyanide.

Crystals obtained by slow evaporation of solution over H_2SO_4 .
Half natural size.

FIG. 3.



Potassium α -ferrocyanide.

Photo-micrograph (H. Priestman).

[To face p. 1023.

solution of potassium β -ferrocyanide was allowed to remain in a basin placed in a desiccator over sulphuric acid, in a few days the desiccator was filled with a moss-like, efflorescent growth of crystals. This was caused by the mother liquor creeping over the surface of the crystals as they were deposited at the edge of the liquid. The crystallisation then proceeded over the interior and exterior of the basin, and on the walls of the desiccator. Potassium α -ferrocyanide did not behave in this way. A similar difference in the capillary properties of the crystals of potassium α - and β -ferricyanides was recorded by Locke and Edwards (*loc. cit.*, p. 198).

Colour.—Potassium α -ferrocyanide is lemon-yellow when the crystals are large, and pure white when the crystals are very small. Potassium β -ferrocyanide is orange-coloured when the crystals are large and transparent, and amber-coloured when seen in bulk. It is cream-coloured when the crystals are very small. The difference in colour persists in solution, the β -ferrocyanide giving a more intensely coloured solution than the α -ferrocyanide. When one modification is transformed into the other in solution, a corresponding change in colour is observed.

Density.—The densities were determined in carbon tetrachloride at 20°. The specimens were obtained by precipitation of a cold aqueous solution with alcohol, in order to ensure homogeneity of the trihydrate (compare Müller and Diefenthaler, *Zeitsch. anorg. Chem.*, 1910, **67**, 418).

No.	1.	2.	3.	4.	5.	6
D 20°/4°	1.882	1.883	1.882	1.888	1.889	1.890

1, 2, and 3 were potassium β -ferrocyanide, obtained as described in preparation (2) above (p. 1021), the acidified solution having been allowed to remain for one, two, and three days respectively before precipitation with alcohol. Number 4 was Kahlbaum's ferrocyanide dissolved in water, and precipitated by alcohol. 5 and 6 were both α -ferrocyanide obtained by the method given above, the solution containing potassium cyanide having been allowed to remain for one day and four days respectively before precipitation with alcohol.

The difference in density is analogous to that observed by Levy for the isomeric barium platinocyanides (*Trans.*, 1908, **93**, 1446). It is evident from Levy's work that the green platinocyanides correspond with the α -ferrocyanides, and the yellow platinocyanides with the β -ferrocyanides.

Solubility.—Three preparations of each form were investigated. The determinations were made at 20°, a weighed quantity of the saturated solution being titrated with *N*/10-permanganate. The

results are expressed as grams of potassium ferrocyanide trihydrate in 100 grams of the saturated solution at 20°:

α .	α .	α .	β .	β .	β .
25.0	25.0	24.9	24.5	24.8	24.6

According to these results, potassium β -ferrocyanide is rather less soluble than potassium α -ferrocyanide at 20°; but the difference is very small, and a much more extensive series of observations would be required to determine this difference accurately. Locke and Edwards state that potassium β -ferricyanide is more soluble than potassium α -ferricyanide, but they do not give any data.

Precipitation Reactions.—The precipitation reactions of the α - and β -ferrocyanides are not so distinctive as those of the α - and β -ferricyanides described by Locke and Edwards. The insoluble ferrocyanides may be divided into two classes according to their colour. The first class includes those in which the yellow colour of the ferrocyanide radicle is present, more or less modified by the metal with which it is combined. The ferrocyanides of lead, zinc, cadmium, nickel, and cobalt are examples. The α -ferrocyanides of this first class are different in colour from the β -ferrocyanides. The second class consists of those ferrocyanides which have an intense and characteristic colour, such as is not usually associated with either the acid or the basic part of the molecule, including the dark blue ferric ferrocyanide, the deep brown ferrocyanides of copper and uranyl, and the bright yellow thallic ferrocyanide. There is no perceptible difference in colour between the α - and β -ferrocyanides of the second class.

With solutions of lead, zinc, and cadmium salts, potassium α -ferrocyanide gives pure white precipitates, and potassium β -ferrocyanide gives yellowish-white precipitates. A more striking difference is observed when the α - and β -ferrocyanides of potassium are added to hot concentrated solutions of barium chloride. A pure white, crystalline precipitate is obtained with the α -ferrocyanide, and a straw-coloured precipitate with the β -ferrocyanide (see $K_2BaFe(CN)_6 \cdot 3H_2O$ below).

Transformation of the α - and β -Ferrocyanides.

When potassium α -ferrocyanide is allowed to remain in aqueous solution for some time it is slowly converted into the β -modification. A similar change is caused by 1 per cent. of acetic acid in twenty-four hours. The effect appears to be due to the hydrogen ions, since other acids (hydrochloric, sulphuric, and nitric) behave in the same way.

The reverse transformation is brought about by cyanides, alkalis, and ammonia, cyanides having the strongest action.

It is probable that in solution the two forms attain a state of equilibrium:



and that acids accelerate the reaction towards the right, whereas cyanides, alkalis, and ammonia increase the reaction towards the left. These transformations are precisely analogous to those observed by Levy with the green and yellow platinocyanides (*loc. cit.*). Locke and Edwards (*loc. cit.*) attributed the change from potassium α -ferricyanide to potassium β -ferricyanide in the presence of acids to the effect of the hydrogen ions. They do not appear to have studied the conditions of the reverse transformation, except for the observation that the β -ferricyanides readily change into the α -salts, especially on heating. I found, however, that potassium β -ferricyanide prepared according to their method was rapidly converted into α -ferricyanide when its solution was treated with a little potassium cyanide, potassium hydroxide, or ammonia. The effect of these reagents was beautifully seen in the colour change from the reddish-violet β -ferricyanide to the bright yellow α -ferricyanide, as well as in the precipitation reactions of the solution, before and after treatment.

In addition to the potassium salt, the following seven ferrocyanides have been obtained in the two modifications, which are related to each other in the same way as the potassium α - and β -ferrocyanides. The two forms when soluble in water give differently coloured solutions. These undergo the same transformations and changes in colour when treated with acids and cyanides respectively, as were found with the solutions of the potassium salts. It should be observed that in the salts of sodium, potassium, ammonium, and caesium the difference in colour of the two modifications, and also the colour change on transformation in solution, become more strongly marked with increase in the atomic volume of the positive atoms, being least with the sodium salts, and greatest with the caesium compounds.

Sodium Ferrocyanides, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$.

Pebal (*Annalen*, 1886, **233**, 165) describes the salt as crystallising in large, transparent crystals, of the colour of sulphur crystallised from carbon disulphide. Bunsen (*Pogg. Ann.*, 1835, **36**, 413) refers to the colour as "hell weingelb."

Sodium α -Ferrocyanide.—The preparation was made from 20 grams of Kahlbaum's sodium ferrocyanide and 0.2 gram of sodium cyanide in 100 c.c. of water, the procedure being the same

as with potassium α -ferrocyanide. A pure white, crystalline powder was obtained, which was collected, and dried with alcohol and ether. When recrystallised from warm water it gave large, pale yellow crystals.

Sodium β -Ferrocyanide was prepared by the action of 2 c.c. of dilute acetic acid (1 vol. of glacial acid made up to 10 vols. with water) on a cold solution of 20 grams of Kahlbaum's sodium ferrocyanide in 100 c.c. of water, in the same way as described for potassium β -ferrocyanide (preparation (2) above, p. 1021).

The sodium β -ferrocyanide was obtained as a yellowish-white powder, which on recrystallisation gave large, bright yellow crystals.

Analysis:

	Required for $\text{Na}_4\text{Fe}(\text{CN})_6, 10\text{H}_2\text{O}$.	Found, α .	Found, β .
Fe	11.54	11.62	11.59
N	17.36	17.01	17.37
H_2O	37.22	36.84	36.85

Ammonium Ferrocyanides, $(\text{NH}_4)_4\text{Fe}(\text{CN})_6, 3\text{H}_2\text{O}$.

The ammonium ferrocyanide was prepared by neutralising hydrogen ferrocyanide with ammonia, and evaporating the filtered solution in a vacuum over potassium hydroxide. The salt was obtained in very thin, greenish-yellow plates.

Ammonium α -Ferrocyanide:—Five and a-half grams of the preparation and 0.05 gram of sodium cyanide were dissolved in 5 c.c. of water. After twenty-four hours the liquid was decanted from a small quantity of blue precipitate, and poured into a large volume of alcohol, when the ammonium α -ferrocyanide was obtained in yellowish-white crystals. Bunsen's preparation (*Pogg. Ann.*, 1835, 36, 404) was evidently α -ferrocyanide, the colour being "weiss, ins Gelbliche spielend."

Ammonium β -Ferrocyanide:—This salt was prepared from 5.5 grams of the ammonium ferrocyanide, 5 c.c. of water, and 0.5 c.c. of dilute acetic acid (1 vol. of glacial acid diluted to 10 vols. with water). The mixture was allowed to remain for twenty-four hours in a small, tightly-stoppered cylinder, and was then precipitated by pouring into a large volume of alcohol. The ammonium β -ferrocyanide separated as a mass of bright amber-coloured crystals, which readily became green on exposure to light. Analysis:

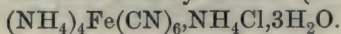
	Required for $(\text{NH}_4)_4\text{Fe}(\text{CN})_6, 3\text{H}_2\text{O}$.	Found, α .	Found, β .
H_2O	16.0	16.8	16.0
N	41.4	40.0	40.3

The low percentage of nitrogen was due to the presence of a

small quantity of potassium, probably derived from the hydrogen ferrocyanide used in the preparation of the salts.

Double Salts of Ammonium Ferrocyanide and Ammonium Chloride,
 $(\text{NH}_4)_4\text{Fe}(\text{CN})_6, 2\text{NH}_4\text{Cl}$.

The double salt was described by Bunsen (*loc. cit.*) as



Etard and Bémont (*Compt. rend.*, 1885, **100**, 108) give the formula $(\text{NH}_4)_4\text{Fe}(\text{CN})_6, 2\text{NH}_4\text{Cl}$, which is confirmed by the present experiments.

The preparations were made from Kahlbaum's ammonium ferrocyanide. This also contained a little potassium, the effect of which is seen in the analyses.

α-Salt:—Fifteen grams of ammonium ferrocyanide were dissolved in 15 c.c. of water, and 0.15 gram of sodium cyanide was added to the solution, which was allowed to remain twenty-four hours. It was then mixed with a solution of 7.5 grams of ammonium chloride in 12 c.c. of warm water. The double salt separated on cooling as a yellowish-white, crystalline powder.

β-Salt:—Fifteen grams of ammonium ferrocyanide in 13 c.c. of water were mixed with 1.5 c.c. of diluted acetic acid (1 vol. of glacial acid in 10 vols.). The solution was placed for twenty-four hours in a stoppered cylinder, which it filled completely, and was then mixed with a solution of 7.5 grams of ammonium chloride in 12 c.c. of warm water. The *β*-salt separated as a deep amber-coloured, crystalline powder. Analysis:

	Required for $(\text{NH}_4)_4\text{Fe}(\text{CN})_6, 2\text{NH}_4\text{Cl}$	Found, <i>α</i> .	Found, <i>β</i> .
N	42.9	41.8, 41.8	42.3
Fe	14.27	14.02	14.05

These salts show the difference in colour of the *α*- and *β*-ferrocyanides to the greatest extent of any which have been prepared. When the mother liquors from the above-mentioned preparations were evaporated over sulphuric acid in a vacuum, very large, transparent crystals were obtained. The crystals of the *α*-double salt were pale orange, and the crystals of the *β*-double salt were brown. The *β*-double salt resembled ammonium *β*-ferrocyanide in the ease with which it became green on exposure to light. The *α*-compounds also became green, but more slowly.

Cæsium Ferrocyanides.

Cæsium hydroxide was neutralised with hydrogen ferrocyanide, and the filtered solution was concentrated on the water-bath and precipitated with alcohol.

The α - and β -cæsium ferrocyanides were obtained from this preparation by the method described above for the potassium salts (p. 1020).

When dehydrated in the steam-oven, the α -salt lost 12.0 per cent. of water, and the β -salt 12.2 per cent. $2\text{Cs}_4\text{Fe}(\text{CN})_6 \cdot 11\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.8$, and $\text{Cs}_4\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 12.7$ per cent. Nitrogen was determined in the dehydrated salts.

	Required for $\text{Cs}_4\text{Fe}(\text{CN})_6$.	Found, α .	Found, β .
N	11.3	11.4	11.3

The difference in colour of equivalent solutions of the cæsium compounds, and the colour change when one modification is transformed into the other, are very marked, and more distinctive than the differences observed with the sodium and potassium compounds.

Potassium Barium Ferrocyanides, $\text{K}_2\text{BaFe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.

Bunsen described the salt $\text{K}_2\text{BaFe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, but did not refer to the colour (*Pogg. Ann.*, 1835, **36**, 404). Wyruboff gave the formula with $5\text{H}_2\text{O}$, also without reference to the colour (*Ann. Chim. Phys.*, 1870, [iv], **21**, 279). The salts obtained in the present investigation have Bunsen's formula.

The α -salt was prepared by mixing boiling solutions of 3 grams of crystallised barium chloride in 6 c.c. of water, and 6 grams of potassium α -ferrocyanide in 7.5 c.c. of water. The salt separated on cooling as a pure white, crystalline deposit, leaving a pale yellow mother liquor.

The β -ferrocyanide was prepared in the same way from potassium β -ferrocyanide. It was obtained in straw-coloured crystals, which left a bright yellow mother liquor.

	Required for $\text{K}_2\text{BaFe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.	Found, α .	Found, β .
N	17.5	17.6	17.8
Ba	28.53	28.68	28.53

Potassium Magnesium Ferrocyanides, $2\text{K}_2\text{MgFe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$.

These salts were prepared by mixing boiling solutions of 6 grams of the respective potassium ferrocyanides in 100 c.c. of water, and 3 grams of magnesium chloride hexahydrate in 100 c.c. of water. The α -ferrocyanide was pure white, and the β -ferrocyanide cream-coloured.

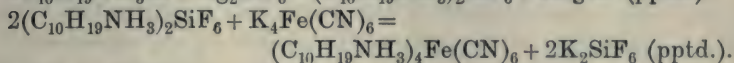
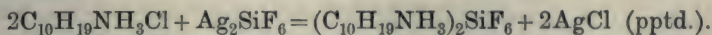
	Required for $2\text{K}_2\text{MgFe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$.	Found, α .	Found, β .
N	22.3	22.5, 22.4	22.4
H_2O	16.7	16.5	—

Robinson obtained the anhydrous compound $K_2MgFe(CN)_6$ by mixing cold concentrated solutions of potassium ferrocyanide and magnesium chloride (Trans., 1909, 95, 1353).

l-Menthylammonium Ferrocyanides.

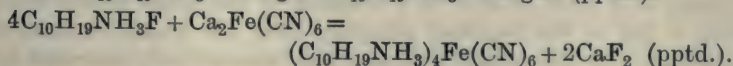
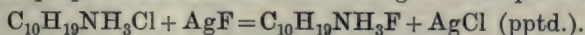
For reasons given below (p. 1033), it was thought desirable to prepare the ferrocyanide of an optically active base, and to determine the specific rotation of the two modifications. For this purpose Professor J. B. Cohen suggested the study of *l*-menthylammonium ferrocyanide. I am also very much indebted to Professor Cohen for a quantity of pure *l*-menthylammonium chloride, with which the preparations were made, and for the use of the polarimeter in his laboratory in the Leeds University. A number of methods were attempted for the preparation of *l*-menthylammonium ferrocyanide, two of which may be described:

(1) It was proposed to obtain the salt by the two precipitation reactions:



A calculated amount of silver sulphate was boiled with barium silicofluoride and water, in order to prepare a solution of silver silicofluoride. In this process partial decomposition took place, a mixture of silver silicofluoride and silver fluoride being obtained. The solution was precipitated in the cold with *l*-menthylammonium chloride, and the silver chloride was removed by filtration. The filtrate was treated in the cold with an excess of potassium ferrocyanide and calcium ferrocyanide to precipitate silicofluoride and fluoride respectively. The resulting solution of the ferrocyanides of potassium, calcium, and *l*-menthylammonium was evaporated on the water-bath at 25° . The *l*-menthylammonium ferrocyanide separated as an oil, but the evaporation was continued until a dry solid mass remained. This was powdered, and extracted with absolute alcohol. The alcoholic solution was concentrated by evaporation at 25° , and then poured into a large volume of ether. A bright yellow, crystalline precipitate of *l*-menthylammonium β -ferrocyanide was obtained.

(2) The preparation was made according to the equations:



The method of preparation was similar to that already described, but the solid residue of almost pure *l*-menthylammonium ferro-

cyanide was extracted with absolute alcohol in two parts. The first extraction, when precipitated with ether, gave what appeared to be a mixture of the α - and β -ferrocyanides. The residue remaining after this extraction was dissolved in absolute alcohol, and the solution was evaporated over sulphuric acid in a vacuum. Long, pale greenish-yellow needles of *l*-menthylammonium α -ferrocyanide were thus obtained. These contained a molecule of alcohol of crystallisation, which was given off at 60°. The β -ferrocyanide already described did not contain alcohol. Analysis:

		Found.	Required for (C ₁₀ H ₁₉ NH ₃) ₄ Fe(CN) ₆ ·C ₂ H ₅ OH.
(1) α -Salt:	N	15.78	15.88
	EtOH.....	5.39	5.22
		Found.	Required for (C ₁₀ H ₁₉ NH ₃) ₄ Fe(CN) ₆ .
(2) β -Salt:	N	16.95	16.75

The two modifications were very different in appearance and in properties. Their solutions in alcohol or in water were different in colour, dilute solutions of the α -form being almost colourless, whereas equivalent solutions of the β -salt were bright yellow. The colour of solutions of the α -salt was intensified by the addition of a trace of acid. Similarly, solution of the β -modification became paler in colour when treated with cyanides. The α -form could not be recrystallised from warm water, as solutions of the alcoholate and also of the dealcoholated salt deposited an uncrystallisable oil on cooling. The β -modification, on the contrary, separated from aqueous solution in bright yellow needles, or, if the solution was slowly evaporated over sulphuric acid, in long, transparent, deep amber-coloured prisms. Both salts decomposed without melting when heated.

The specific rotations were determined at 17° in absolute alcoholic solution, in order to avoid the effect of ionisation. Owing to the colour of the salts, the observations were rather difficult, and it was not possible to work with a solution of higher concentration than 1 per cent. when using a 2-dcm. tube.

	Vol. of solution.	Weight of salt.	α .	$[\alpha]_D^{17^\circ}$.
(1) α -Salt	50 c.c.	0.540	-0.87°	-42.4°
(2) β -Salt	50 ,,	0.500	0.57	28.5

Assuming these observations to be approximately correct, the addition of a trace of acid to a solution of the α -salt should bring about a fall in the rotation, resulting from the transformation of the α -form into the β -modification. This was actually observed.

The acid was prepared by diluting 0.4 c.c. glacial acetic acid to 10 c.c. with absolute alcohol; 0.1 c.c. of this solution was added

to 25 c.c. of the solution of the α -salt in experiments 3 and 4. The rotations were determined in the freshly prepared solutions, and also after twenty-four hours, a 2-dcm. tube being used.

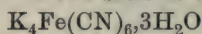
	Vol. of solution.	Weight of salt.	α .	$[\alpha]_D^{17^\circ}$.
(3) α -Salt	50 c.c.	0.501 gram.	-0.81°	-42.6°
„ after 24 hours	50 „	0.501 „	0.65	34.2
(4) α -Salt	25 „	0.261 „	0.81	40.9
„ after 24 hours	25 „	0.261 „	0.63	31.8

It is therefore evident that the conversion of one modification into the other is accompanied by a change in specific rotation, as well as a change in colour.

PART II.

Relationship of the α - and β -Ferrocyanides.

The difference in colour of two salts of the formula



may be due to any of the following causes:

(1) Dimorphism. (Difference in the arrangement of the molecules in the crystal.) (2) Polymerism. (Difference in the state of aggregation of the molecules in the two modifications.) (3) Hydrate isomerism. (Difference in the method of attachment of the three molecules of water of crystallisation in the two forms.) (4) The presence of a coloured impurity in the β -modification. (5) Structural isomerism of the molecule $\text{K}_4\text{Fe}(\text{CN})_6$. (Cyanide and isocyanide isomerism is the only possibility of this kind.) (6) Stereoisomerism of the molecule $\text{K}_4\text{Fe}(\text{CN})_6$, as suggested at the commencement of the paper.

These various possibilities will be discussed separately:

Dimorphism.—If the α - and β -ferrocyanides were dimorphous, then the difference in properties should disappear when the crystal structure is destroyed by solution or by dehydration. It has already been shown, however, that the difference in properties persists in solution. It was also found that the two potassium ferrocyanides when dehydrated over sulphuric acid were still different in colour, and when the dehydrated salts were recrystallised from warm water, the α - and β -ferrocyanides were regenerated unchanged. The salts, therefore, are not dimorphous.

Polymerism.—Since the difference in properties persists in solution, freezing-point determinations should give a difference in molecular weight if one modification were a polymeride of the other. A series of molecular-weight determinations was made with the potassium salts. As shown in Fig. 4, when the results are plotted with molecular weights as abscissæ and concentrations as ordinates,

only one curve is obtained. There is, therefore, no difference in the state of aggregation of the α - and β -ferrocyanides.

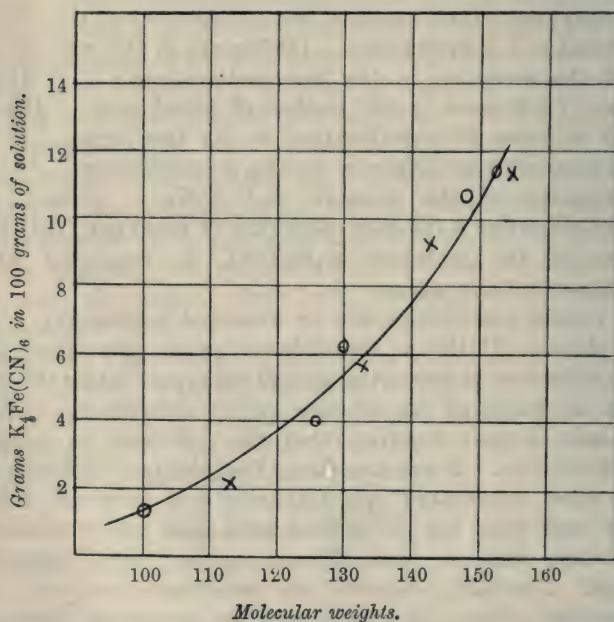
α -Ferrocyanide.

<i>w.</i>	<i>W.</i>	$\Delta T.$	M. W.	Grams $K_4Fe(CN)_6$ in 100 grams of solution.
0.487	11.76	0.62	126	4.0
0.775	11.80	0.95	130	6.2
0.644	5.37	1.52	148	10.7
1.747	13.55	1.58	153	11.4
0.169	13.32	0.24	100	1.3

β -Ferrocyanide.

0.255	11.20	0.38	113	2.2
0.659	11.26	0.83	133	5.6
1.165	11.33	1.35	143	9.3
1.744	13.74	1.54	155	11.3

FIG. 4.



O = α -Ferrocyanide. X = β -Ferrocyanide.

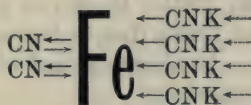
Hydrate Isomerism:—The difference is evidently not the result of hydrate isomerism, since ferrocyanides have been described above with various amounts of water of crystallisation (3, 6, and 10

molecules), and even without water of crystallisation (the *l*-menthylammonium compounds), but still capable of existing in the two modifications. Again, the difference does not disappear on dehydration of the two potassium salts, as it would if the salts were hydrate isomerides.

Impurity:—It was shown by the analyses of the potassium salts (p. 1022) that no appreciable amount of impurity was present in the β -modification. The deeper colour of the β -ferrocyanides might still be due, however, to a trace of very highly coloured impurity, which could not be detected by analysis. If this were the case, then the α - and β -modifications of the ferrocyanide of an optically active base should have the same specific rotation, whereas if the difference in the α - and β -ferrocyanides were due to structural isomerism or stereoisomerism, a difference in specific rotation would be expected. For this reason the *l*-menthylammonium salts were investigated, as already described. They were found to differ greatly in specific rotation, and the transformation of the α -ferrocyanide into the β -salt was accompanied by a corresponding change in rotation. It therefore follows that in the *l*-menthylammonium ferrocyanides the *l*-menthylammonium radicles are either combined with different groups in the two salts (that is to say, the salts are cyanide and isocyanide respectively), or the *l*-menthylammonium groups are situated in different positions in the two modifications, that is, the α - and β -ferrocyanides are stereoisomeric.

Cyanide and isoCyanide Isomerism:—If the salts were cyanide and isocyanide, they should display considerable differences in chemical and physical properties. The chemical and physical properties are very similar, however, as was shown by the detailed investigation of the two potassium salts already described.

Stereoisomerism therefore appears to be the most probable explanation of the difference of the α - and β -ferrocyanides, and accounts satisfactorily for the phenomena which have been observed. Two salts of the formula suggested in the previous paper (Trans., 1908, 93, 1564):



should exist in two stereoisomeric forms:

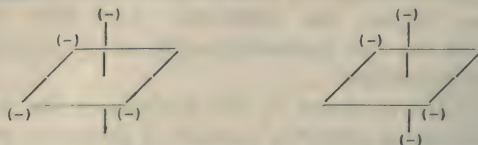


1, 2, 3, 4.



1, 2, 6, 4.

It is evident that in solution these forms would give stereoisomeric anions:



which agrees with the observation that the difference in properties persists in solution.

Direct evidence in favour of stereoisomerism is furnished by:

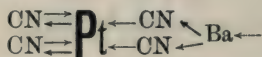
(1) The ease with which one modification can be transformed into the other, and by the opposite action of acids and bases in effecting this transformation, which is analogous to their influence on the conversion of the *syn*- and *anti*-aldoximes (Hantzsch, *Grundriss der Stereochemie*, 2nd ed., p. 150).

(2) The increasing difference of the α - and β -ferrocyanides with increase in the atomic volume of the positive atoms. It is evident that the effect of transferring an atom from position (3) to position (6) and vice versa will be all the greater the greater the volume occupied by that atom.

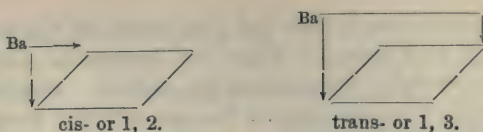
(3) The difference in the α - and β -ferrocyanides is not so great as that between the α - and β -ferricyanides of Locke and Edwards. A study of the formulæ shows that the effect of moving one potassium atom out of three from position (3) to position (6) in the ferricyanides will be greater than that of the corresponding change in position of one potassium atom out of four in the ferrocyanides.

An absolute proof that the salts are stereoisomeric, and not cyanide and isocyanide, can only be obtained by preparing in two modifications other salts which do not contain cyanogen groups, but which are otherwise similarly constituted to the ferrocyanides. I intend to continue the investigation in this direction. Attention may be directed to the fact that many platinichlorides are said to be dimorphous (Schryver, *Proc.*, 1891, **7**, 39; Trobridge, *J. Soc. Chem. Ind.*, 1909, **28**, 230). It is not impossible that some of these instances may be really due to isomerism.

In conclusion, it may be observed that the platinocyanides, such as barium platinocyanide:



should exist in two stereoisomeric forms if Werner's "square" configuration for plato-compounds is adopted. The formulæ would be:



The yellow and green platinocyanides of Levy (*loc. cit.*) may be explained in this way.

I should like to express my thanks to Professor A. Smithells, F.R.S., and to Professor J. B. Cohen, F.R.S., for the interest which they have taken in this investigation.

CLECKHEATON.

CVIII.—*The Interaction of Copper and Nitric Acid in Presence of Metallic Nitrates. Part II.*

By EDWARD HENRY RENNIE, M.A., D.Sc., and WILLIAM TERNENT COOKE, D.Sc.

IN a previous paper (Trans., 1908, **93**, 1162), it was shown that the solution of copper in diluted nitric acid may be either accelerated or retarded by the addition of metallic nitrates. The experiments therein described were made at a temperature of about 59°, and the acid used was 2*N*. At that temperature, and with that concentration, it was shown that lithium and sodium nitrates greatly accelerate solution, potassium nitrate has little or no influence, whereas rubidium and caesium nitrates have a retarding effect. In these experiments no notice was taken of the fact that when large quantities of nitrates are dissolved in nitric acid the volume of the solution is considerably increased, and the concentration* of the nitric acid (and also of any nitrous acid, copper nitrate, or other products formed during the solution) therefore considerably diminished. Whilst this fact could not explain acceleration, it might partly explain retardation, and the question arises whether the apparent inactivity of potassium nitrate may not really indicate acceleration just about counterbalanced by a retardation due to diminished concentration. Further, whilst diminished concentration of the nitric acid brought about by dilution with water would obviously retard solution, it seemed probable (inasmuch as the solution of copper has been shown by Veley and others to be almost certainly conditioned by the

* By concentration is here meant, of course, the quantity of nitric acid per c.c. of solution.

formation of nitrous acid) that the diminution of the concentration of the nitrous acid brought about by increasing the volume of nitric acid used would also produce retardation. Similarly, in such a case, although to a less extent, the acceleration shown by us to be due to the formation of copper nitrate would be lessened by the diminished concentration of that substance throughout the period of reaction. Again, increasing the surface of the copper (whilst retaining the same volume of nitric acid) might be expected to lead to a more rapid development, and consequently an increased concentration of nitrous acid, and therefore a more rapid solution.

The following experiments illustrate these effects. In them and in all others described in this paper, the pieces of copper were 1.96 sq. cm. in area, and weighed 0.083 gram (within one milligram). These were cut from electrolytic copper, not the same as that used in the experiments described in the previous paper, but of almost exactly the same thickness. They were cleaned by washing well, first with ether, then with alcohol, then with very dilute nitric acid (about 1 c.c. commercial acid and 300 c.c. water), and finally with distilled water. They were then, without handling by the fingers, pressed between folds of Swedish filter paper, allowed to dry in the air, and placed in a well-closed bottle.

The temperatures are correct to half a degree. The times are expressed in minutes and decimals of a minute, but in the longer periods only to the nearest half-minute. The apparatus was the same as that previously used, except that the stirrers were moved by a small electric motor, to which was attached a dial for counting revolutions, so that the rate of stirring could be kept constant by the aid of a shunt resistance. That this is a matter of some importance was shown in our previous paper (*loc. cit.*).

No. of experiment.	No. of pieces of copper.	Strength of acid.	Volume of acid.	Temperature.	Times of complete solution.
1	1	2 <i>N</i>	10 c.c.	63°	30.0—34
2	1	2 <i>N</i>	20 „	63	47.0—48
3	2	2 <i>N</i>	10 „	63	18.5—18
4	1	2 <i>N</i>	10 „	79	9
5	1	2 <i>N</i>	15 „	79	10
6	1	2 <i>N</i>	20 „	79	11

These are only a few of a number of experiments tried with similar results, and they clearly show the effect above discussed. Comparing experiment 2 with experiment 1, and experiments 5 and 6 with experiment 4, it is seen that increasing the volume of the nitric acid has a retarding effect. Comparing experiment 3 with experiment 2, it is clear that doubling the surface of the copper has a great accelerating effect, in spite of the fact that twice the weight of copper has to be dissolved. These results

therefore are sufficient to prove the correctness of our anticipations, and they seem to show that in our previous experiments with potassium nitrate, the apparent inactivity of the latter may have been caused by the increase of volume (and consequent lessening of concentration of nitric acid, nitrous acid, and copper nitrate) due to its solution in the acid. We shall return to this point later.

The experiments in our previous communication (*loc. cit.*) having all been made with the same concentration of acid and at the same temperature, it was thought advisable to extend the investigation to include other temperatures and other concentrations, and it soon became apparent that potassium nitrate either accelerates or retards according to the conditions of temperature and concentration. The same is true of rubidium and caesium nitrates (see tables III, VIII, and X), but with sodium nitrate there is always acceleration under any conditions yet tried. With potassium nitrate and with the same concentration of acid, the lower the temperature the less is the acceleration (it often becomes retardation). The higher the temperature the greater is the acceleration, and the same seems to be true of rubidium and caesium nitrates (see tables III, VIII, IX, and X). With the same temperature, so far as the imperfect data allow us to judge, increase of concentration of acid tends to lessen acceleration.

In commencing this new series of experiments with potassium nitrate, determinations were first made, using the same thermometer as before, at a temperature supposed to be the same (namely, 59° , as indicated by that thermometer), and with the same concentration of acid ($2N$), in order to confirm previous results with the new sample of copper and with fresh acid, but there now appeared to be a slight but distinct acceleration as contrasted with the inactivity or possible slight retardation before recorded. It was then found that the mercury in the thermometer had partly separated into the upper part of the capillary (it had been in constant use for a long time with different samples of copper under different conditions), and on readjustment the true temperature was now found to be 62.5° . This accounts for the observed difference in the results, which are incorporated in table V. All attempts to secure anything like exact agreement in times of solution, under the same conditions, have, however, been in vain, in spite of every care in cleaning the copper, in adjusting temperature, and in maintaining a constant rate of stirring. Occasionally, too, altogether abnormal results are obtained, which we can only ascribe at present to irregularities in the physical condition of the copper.

The tables which follow give the results obtained with acids of varying strength and at different temperatures. The quantities

of nitrate added are, as before, expressed in decimals of one equivalent in grams.

TABLE I.

N-Acid. Temperature 62.5°. Volume of Acid 10 c.c.

Acid only.	0.02 equiv. KNO ₃ .	0.04 equiv. KNO ₃ .	0.04 equiv. NaNO ₃ .
98	72	75	43.5
89	70	74	41.0
85	72	70	—
100	—	68	—
95	—	69	—
—	—	74	—
Mean 93.5	Mean 71.3	Mean 72	Mean 42.2

TABLE II.

N-Acid. Temperature 78.5°. Volume of Acid 10 c.c.

Acid only.	0.02 equiv. KNO ₃ .	0.04 equiv. KNO ₃ .	0.04 equiv. NaNO ₃ .
61	29	27	12.0
50	31	28	12.9
55	27	27	—
—	27	—	—
Mean 55.3	Mean 28.5	Mean 27.3	Mean 12.5

TABLE III.

N-Acid. Temperature 98—100°. Volume of Acid 10 c.c.

Acid only.	0.02 equiv. KNO ₃ .	0.04 equiv. KNO ₃ .	0.02 equiv. RbNO ₃ .	0.04 equiv. RbNO ₃ .	0.02 equiv. CsNO ₃ .	0.04 equiv. CsNO ₃ .	0.04 equiv. NaNO ₃ .
33	14	10.5	18	16	18.3	14.3	1.6
32	14	10.0	20	—	18.3	—	1.5
32	14	—	—	—	—	—	—
Mean 32.3	Mean 14	Mean 10.2	Mean 19	16	Mean 18.3	14.3	Mean 1.55

In these and in other experiments at 98—100°, the water in the bath was kept gently boiling.

TABLE IV.

2*N*-Acid. Temperature 48.5°. Volume of Acid 10 c.c.

Acid only.	0.02 equiv. KNO ₃ .	0.04 equiv. KNO ₃ .	0.04 equiv. NaNO ₃ .
70.0	83.0	94	37.5
78.0	79.5	93	35.0
75.0	92.0	109	—
72.0	—	—	—
76.0	—	—	—
68.5	—	—	—
Mean 73.3	Mean 84.8	Mean 98.7	Mean 36.2

TABLE V.

2*N*-Acid. Temperature 62.5°. Volume of Acid 10 c.c.

Acid only.	0.02 equiv. KNO ₃ .	0.04 equiv. KNO ₃ .	0.04 equiv. NaNO ₃ .
28.5	25.5	25.5	8.5
30.0	25.0	26.0	9.0
27.0	26.0	26.0	—
29.0	27.5	26.0	—
27.5	—	25.0	—
28.5	—	25.5	—
27.5	—	27.0	—
29.5	—	27.0	—
27.0	—	—	—
29.0	—	—	—
30.0	—	—	—
27.0	—	—	—
Mean 28.4	Mean 26.0	Mean 26.0	Mean 8.7

TABLE VI.

2*N*-Acid. Temperature 78.5°. Volume of Acid 10 c.c.

Acid only.	0.02 equiv. KNO ₃ .	0.04 equiv. KNO ₃ .
8.6	6.5	6.3
8.7	6.7	6.6
9.0	6.5	7.0
9.0	—	6.6
9.5	—	7.0
9.0	—	—
Mean 8.9	Mean 6.6	Mean 6.7

It will be observed that in the experiments described in tables I, II, V, and VI, doubling the proportion of nitrate seems to produce practically no increased effect. The addition, however, of 0.02 of an equivalent and still more of 0.04 equivalent (2.02 and 4.04 grams respectively) to 10 c.c. of acid has a marked effect in increasing the total volume, and therefore, as already indicated, of decreasing the concentration of the nitric acid and of the nitrous acid and copper nitrate formed. This increase in volume was approximately measured under the conditions in table VI, and experiments were made in which sufficient water was added to the original 10 c.c. of acid to make the volume, at the temperature of the experiments, equal to the volume of the acid plus nitrate at the same temperature. Under these conditions, the times of solution in the diluted acid were as follows:

1. Volume made up to equal that produced by addition of 0.02 equivalent of potassium nitrate in grams:

10.5, 10.5, 10.6, 10.6 minutes.

2. Volume made up to equal that produced by addition of 0.04 equivalent of potassium nitrate in grams:

15.6, 15.7 minutes.

In further elucidation of this point, two experiments were made, in which the quantities of nitrate (0.02 and 0.04 equivalent in grams) were placed in the tubes, 6.7 c.c. 3*N*-acid added (=10 c.c. 2*N*-acid), the whole raised to the temperature of the bath (78.5°), and then water slowly added, until the volume was as nearly as possible the same as that occupied by the 10 c.c. of 2*N*-acid at the same temperature, the concentration of the acid thus being the same as in 10 c.c. of 2*N*-acid at the same temperature. The times of solution were diminished to 4.7 and 3.3 minutes respectively, as against 6.6 minutes in table VI.

It is, of course, not contended that these experiments lead to any exact comparisons as regards the effect of the expansion due to dissolved nitrate. It is clear that increase of volume caused by addition of nitrate is not the same thing as increase of volume caused by addition of water. The relative masses of acid and water are not the same in the two cases, although the concentration of the acid is the same. Exact comparison could only be obtained either by the addition of some absolutely neutral liquid (if such exists), or by the impossible process of increasing the volume of the acid without increase of temperature, and without addition of anything, to that occupied by the acid plus nitrate. Similar considerations apply to those experiments in which the volume of the acid plus nitrate is kept down to that occupied by the acid. Nevertheless, the experiments serve to show the great influence of changes in concentration of the various constituents of the solution. Almost certainly, therefore, the apparent absence of any effect, above referred to, when the quantity of nitrate is doubled, is due to a balancing between acceleration due to increased mass of nitrate and retardation due to decreased concentration.

TABLE VII.

2*N*-Acid. Temperature 98—100°. Volume of Acid 10 c.c.

Acid only.	0.02 equiv. KNO ₃ .	0.04 equiv. KNO ₃ .	0.04 equiv. NaNO ₃ .
5.2	3.05	2.5	1.5
5.0	3.08	2.5	1.5
—	3.20	2.6	—
Mean 5.1	Mean 3.10	Mean 2.53	Mean 1.5

TABLE VIII.

 3*N*-Acid. Temperature 39°. Volume of Acid 10 c.c.

Acid only.	0.04 equiv. KNO ₃ added, but only about five-sixths dissolved.	0.02 equiv. CsNO ₃ added, but only about three-quarters dissolved.	0.02 equiv. RbNO ₃ .	0.02 equiv. LiNO ₃ .	0.04 equiv. NaNO ₃ .
104	166.0	No visible	No visible	—	35
118	152.0	action in	action in	39	35
100	145.5	five hours.	five hours.	—	—
127	145.5			—	—
Mean 112.2	Mean 152.2				Mean 35

TABLE IX.

 3*N*-Acid. Temperature 48.5°. Volume of Acid 10 c.c.

Acid only.	0.04 equiv. KNO ₃ .	0.02 equiv. RbNO ₃ .	0.02 equiv. CsNO ₃ .	0.04 equiv. NaNO ₃ .
28.0	40.0	44.3	66.6	11.1
29.0	52.0	41.2	64.5	10.3
34.0	36.0	—	—	—
32.0	51.5	—	—	—
31.5	43.0	—	—	—
33.0	35.5	—	—	—
30.0	54.0	—	—	—
36.0	40.5	—	—	—
34.0	44.0	—	—	—
33.0	72.0	—	—	—
33.0	38.0	—	—	—
28.5	70.0	—	—	—
Mean 31.8	Mean 48.0	Mean 42.7	Mean 65.5	Mean 10.7

The results in table IX are less satisfactory than those in any other. The figures in the first and second column are typical of those obtained in a large number of experiments which were made in the vain hope of finding some source of error and of getting more consistent results. Apparently, however, under these special conditions, a sort of critical state occurs as regards production of nitrous acid. Sometimes the reaction starts and goes on normally, but often it is greatly delayed. It was observed that, if in one of the delayed cases the stirring was stopped for a second or two, reaction at once commenced, and then proceeded as usual when stirring recommenced. Similar but more marked results of the same kind have been observed in some preliminary experiments with silver and nitric acid with certain temperatures and concentrations, and we hope to investigate this phenomenon at a later date.

TABLE X.

3*N*-Acid. Temperature 62·5°. Volume of Acid 10 c.c.

Acid only.	0·02 equiv. KNO ₃ .	0·04 equiv. KNO ₃ .	0·02 equiv. RbNO ₃ .	0·04 equiv. RbNO ₃ .	0·02 equiv. CsNO ₃ .	0·04 equiv. CsNO ₃ only three-quarters dissolved.	0·04 equiv. NaNO ₃ .
8·0	7·9	8·5	8·0	10·5	8·5	10·7	3·7
8·0	7·9	9·5	8·2	10·9	9·0	—	3·7
8·1	7·5	—	—	—	—	—	—
7·7	8·0	—	—	—	—	—	—
Mean 7·95	Mean 7·8	Mean 9·0	Mean 8·1	Mean 10·7	Mean 8·7	—	Mean 3·7

Here the apparent effect produced by, for example, 0·02 equivalent of potassium, rubidium, and caesium nitrates is so very small that probably in all these cases there is really acceleration neutralised by diminished concentration due to solution of nitrate.

Owing to pressure of routine work, these investigations cannot be carried on without serious interruptions. It is thought better therefore to offer these results, imperfect though they are, rather than to risk long delay. The results so far seem to us at least not to invalidate the tentative opinions put forward in our previous paper, namely, that "when a nitrate is added to dilute nitric acid, there is competition between the acid and water," both tending to combine with the salt. The result of such competition would undoubtedly be much modified by alterations in temperature and in the relative masses of acid and water.

Summary.

1. Experiments on the interaction of copper and nitric acid in presence of metallic nitrates have been extended to other temperatures and other concentrations of acid than those previously used.

2. Whereas potassium nitrate appeared from previous experiments to have little or no effect, and rubidium and caesium nitrates to have distinct retarding effects, it is now shown that all these nitrates may either accelerate or retard solution according to temperature and concentration of acid.

3. The retarding effect is, however, probably partly due to the increased volume, and consequent diminution of concentration of acid and products of change, due to solution of the nitrates.

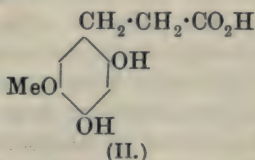
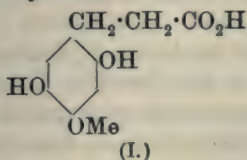
CIX.—*The Constitution of Scopoletin.*

By CHARLES WATSON MOORE.

Two monomethyl ethers of aesculetin (4:5-dihydroxycoumarin) are known, which melt at 184° and 204° respectively. One of these (m. p. 204°) was designated as scopoletin by Eykman (*Rec. trav. chim.*, 1884, **3**, 171), who first isolated it from the rhizome of *Scopolia japonica*. This substance also occurs in *Atropa Belladonna* (Kunz-Krause, *Arch. Pharm.*, 1885, **223**, 701), in *Gelsemium* (Wormley, *Amer. J. Pharm.*, 1870, **42**, 1; and Moore, *Trans.*, 1910, **98**, 2223), in the bark of *Prunus serotina* (Power and Moore, *Trans.*, 1909, **95**, 243), and in jalap (Power and Rogerson, *J. Amer. Chem. Soc.*, 1910, **32**, 93). On account of its occurrence in different plants, scopoletin has been variously referred to as "gelseminic acid," "chrysotropic acid," and " β -methylaesculetin," but the latter designation is particularly inappropriate for reasons which have previously been noted (*Trans.*, 1910, **98**, 2224), and it is therefore considered desirable to retain the original name, scopoletin, for the above-mentioned compound.

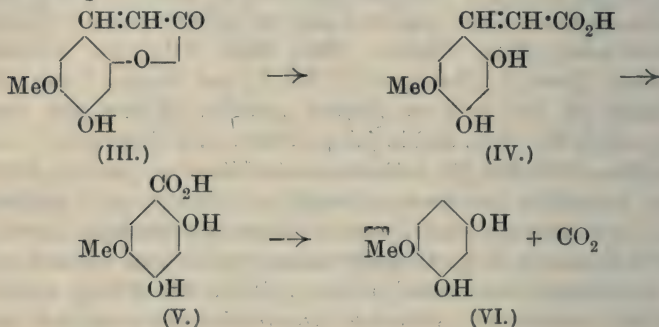
Although scopoletin is known to be a monomethyl ether of aesculetin (Schmidt, *Arch. Pharm.*, 1898, **236**, 236), the position of the methyl group does not appear to have been determined. Kunz-Krause (*Ber.*, 1893, **31**, 1189) refers to this substance as 4-hydroxy-5-methoxycoumarin, but this was apparently only an assumption, as no evidence is cited in support of his statement. A quantity of scopoletin being available, it therefore appeared of interest to ascertain the position of the methyl group in this substance, and thus determine the orientation of both the monomethyl ethers of aesculetin.

On hydrolysis, scopoletin should be converted into the corresponding coumaric acid, from which a dihydroxymethoxyphenylpropionic acid would be formed on reduction. The latter acid would be represented by formula I or II, according as to whether scopoletin were methylated in the 4- or 5-position:



In the former case the two hydroxyl groups would be in the para-position with respect to each other, and it should therefore be possible to obtain the corresponding quinone by oxidation.

On attempting to prepare the substituted coumaric acid from scopoletin by the prolonged action of aqueous potassium hydroxide on the latter, it was found that oxidation took place, with the production of a dihydroxymethoxybenzene. Only two possibilities can here exist, and the product of the reaction must be either 2:5- or 2:4-dihydroxyanisole, according as scopoletin is the 4- or 5-methyl ether of aesculetin. As the phenol obtained was found to be the 2:4-dihydroxy-compound, its formation from scopoletin must be represented as follows:



Scopoletin must, therefore, be 4-hydroxy-5-methoxycoumarin, whilst the other monomethyl ether of aesculetin, melting at 184° , which has only been obtained synthetically, will be 5-hydroxy-4-methoxycoumarin.

The identification of the above-mentioned 2:4-dihydroxyanisole was effected by means of its analysis and melting point, and by the preparation of its *diacetyl* derivative, which melts 30° lower than 2:5-*diacetoxyanisole*.

Attempts to isolate the 2:4-dihydroxy-5-methoxybenzoic acid (V), which must be formed as an intermediate product, were unsuccessful, and it appears probable that this substance, when liberated from its salts, loses carbon dioxide with the formation of the corresponding dihydroxyanisole.

Although the prolonged action of aqueous potassium hydroxide on scopoletin had been found to result only in the formation of a phenol, it has been ascertained that if the alkali is allowed to act for a few minutes only, an almost quantitative yield of 2:4-dihydroxy-5-methoxycinnamic acid is obtained. Sodium derivatives of this acid have already been described by Kunz-Krause (*loc. cit.*), who, however, does not appear to have prepared the free acid. A number of derivatives of this substance have now been prepared, which are described in this paper.

The ease with which scopoletin is hydrolysed is remarkable, as coumarin is only very slowly converted into *o*-coumaric acid by

prolonged boiling with aqueous potassium hydroxide, and the dimethyl ether of aesculetin shows a similar stability.

EXPERIMENTAL.

The scopoletin employed was obtained from the rhizome of *Gelsemium sempervirens*, Aiton (Trans., 1910, **97**, 2223), in which it occurs to the extent of about 0.05 per cent. It forms yellow needles, melting at 204°, and in alkaline solution shows a fine blue fluorescence.

Action of Potassium Hydroxide on Scopoletin.

(1) *Formation of 2:4-Dihydroxyanisole.*

With the endeavour to obtain the coumaric acid corresponding with scopoletin, a quantity (4 grams) of the latter was boiled for nine hours with 50 c.c. of a 45 per cent. aqueous solution of potassium hydroxide. The resulting dark-coloured aqueous solution was acidified, and extracted with ether. The ethereal extract was dried, and the solvent removed, when a dark brown, syrupy liquid was obtained, which showed no tendency to crystallise. The product was therefore distilled under diminished pressure, when the greater part of it passed over as an almost colourless, viscid liquid, which, when dissolved in dry benzene, separated, on keeping, in glistening prisms (1.5 grams), melting at 66–68°. (Found, C=59.8; H=5.9; OMe=22.0. Calc., C=60.0; H=5.7; OMe=22.1 per cent.).

The compound is therefore a dihydroxyanisole, and from its melting point must be 2:4-dihydroxyanisole, the only possible alternative being the 2:5-dihydroxy-compound, which, however, melts at 84°. For the purpose of comparison, a small quantity of the latter was prepared by the reduction of the corresponding quinone, as described by Witt (*Ber.*, 1888, **21**, 605). Methoxyquinone was found to melt at 145°, instead of 140°, as recorded (*loc. cit.*), and possesses no quinone-like odour. On reduction it yields 2:5-dihydroxyanisole, which crystallises from benzene in glistening prisms, melting at 84°, as recorded in the literature (*loc. cit.*).

Further confirmation as to the identity of the above-described compound with 2:4-dihydroxyanisole was obtained by preparing its *diacetyl* derivative, and comparing this with 2:5-*diacetoxyanisole*.

2:4-Diacetoxyanisole.—2:4-Dihydroxyanisole was boiled for a few minutes with acetic anhydride in the presence of a trace of *d*-camphorsulphonic acid. The solution was then poured into water, when, after a time, a crystalline precipitate separated. This

was collected, and recrystallised from methyl alcohol, when it formed glistening prisms, melting at 62—64°:

0.1468 gave 0.3180 CO₂ and 0.0725 H₂O. C=59.0; H=5.5.

0.2142 „ 0.2225 AgI. OMe=13.7.

C₁₀H₉O₄·OMe requires C=58.9; H=5.3; OMe=13.8 per cent.

2:5-Diacetoxyanisole.—This was prepared by the action of acetic anhydride on 2:5-dihydroxyanisole, as in the preceding case. *2:5-Diacetoxyanisole* crystallises from methyl alcohol in glistening, prismatic needles, melting at 93—94°:

0.1258 gave 0.2720 CO₂ and 0.0605 H₂O. C=58.9; H=5.3.

C₁₁H₁₂O₅ requires C=58.9; H=5.3 per cent.

It is therefore evident that the product of the prolonged action of boiling aqueous potassium hydroxide on scopoletin is 2:4-dihydroxyanisole, and the formation of this compound is only possible, as already indicated, if scopoletin is 4-hydroxy-5-methoxycoumarin. Attempts to isolate the corresponding 2:4-dihydroxy-5-methoxybenzoic acid, which must be formed as an intermediate product, were unsuccessful.

(2) Formation of 2:4-Dihydroxy-5-methoxycinnamic Acid.

If scopoletin is dissolved in 10—20 per cent. aqueous potassium hydroxide, and the solution boiled for a few minutes, the lactone grouping is hydrolysed, and the liquid then shows no fluorescence.

A quantity (10 grams) of scopoletin was added to 100 c.c. of boiling 20 per cent. aqueous potassium hydroxide, and the solution boiled for four minutes. The alkaline liquid was then at once cooled, ice added, and acidified by the addition of 40 c.c. of concentrated hydrochloric acid, mixed with an equal volume of ice, the temperature being kept below 10°. After a short time, a yellow, crystalline precipitate separated, which was collected, well washed with ice-water, and dried in a desiccator. The product so obtained amounted to 9 grams. It crystallised from hot water in bright yellow needles, melting and decomposing at 178—180°:

0.5778,* on heating at 110°, lost 0.0468 H₂O. H₂O=8.1.

0.1426 † gave 0.2995 CO₂ and 0.0650 H₂O. C=57.3; H=5.0.

0.1628 † „ 0.1780 AgI. OMe=14.4.

C₁₀H₁₀O₅·H₂O requires H₂O=8.0 per cent.

C₉H₇O₄·OMe requires C=57.1; H=4.8; OMe=14.7 per cent.

The substance is therefore the coumaric acid corresponding with scopoletin, or *2:4-dihydroxy-5-methoxycinnamic acid*, sodium derivatives of which were obtained by Kunz-Krause (*Ber.*, 1898, 31, 1192).

* Air-dried.

† Anhydrous substance.

2:4-Dihydroxy-5-methoxycinnamic acid is sparingly soluble in ether and cold water, but dissolves readily in hot water. It rapidly decomposes on boiling with dilute acids, more slowly with hot water, with loss of carbon dioxide. On heating with acetic anhydride, it loses water, and is converted into acetylscopoletin.

2:4:5-Trimethoxycinnamic Acid.—Ten grams of 2:4-dihydroxy-5-methoxycinnamic acid were dissolved in 100 c.c. of alcohol, and to the solution were added 10 grams of methyl sulphate and then excess of concentrated aqueous potassium hydroxide. The solution was then boiled, acidified, and extracted with ether, the ethereal extracts being subsequently extracted with aqueous ammonium carbonate. The alkaline liquids thus obtained were acidified, extracted with ether, and the ethereal solution concentrated to a small volume, when a substance separated in small, yellow needles. This was collected, and recrystallised from dilute alcohol, when it formed a crystalline mass, melting at 163—165°:

0.1336 gave 0.2970 CO_2 and 0.0725 H_2O . $\text{C}=60.6$; $\text{H}=5.9$.

$\text{C}_{12}\text{H}_{14}\text{O}_5$ requires $\text{C}=60.6$; $\text{H}=5.9$ per cent.

The substance is thus 2:4:5-trimethoxycinnamic acid, and on oxidation it yielded asarylaldehyde (2:4:5-trimethoxybenzaldehyde) and the corresponding asaronic acid.

Reduction of 2:4-Dihydroxy-5-methoxycinnamic Acid.

Formation of 2:4-Dihydroxy-5-methoxy- β -phenylpropionic Acid.

A quantity (5 grams) of 2:4-dihydroxy-5-methoxycinnamic acid was dissolved in about 150 c.c. of aqueous methyl alcohol, and twice the theoretical amount of 3 per cent. sodium amalgam gradually introduced, the mixture being kept acid by the frequent addition of acetic acid. When the reduction was finished, hydrochloric acid, in slight excess, was added, and the solution boiled to remove the excess of methyl alcohol. The aqueous liquid was then extracted with ether, which removed a quantity (3 grams) of a crystalline substance. The latter, on recrystallisation from water, formed small, glistening needles, which melted, when dried in the air, at 68—69°:

0.1158 * gave 0.2216 CO_2 and 0.0640 H_2O . $\text{C}=52.2$; $\text{H}=6.1$.

$\text{C}_{10}\text{H}_{12}\text{O}_5 \cdot \text{H}_2\text{O}$ requires $\text{C}=52.2$; $\text{H}=6.1$ per cent.

This substance is therefore 2:4-dihydroxy-5-methoxy- β -phenylpropionic acid, and, as the analysis shows, it crystallises from its aqueous solution with one molecule of water of crystallisation.

Lactone of 2:4-Dihydroxy-5-methoxy- β -phenylpropionic Acid.—

* Air-dried.

On distilling 2:4-dihydroxy-5-methoxy- β -phenylpropionic acid under diminished pressure, it loses one molecule of water, and is converted into its lactone, which crystallises from water in colourless needles, melting at 155°:

0.1442 gave 0.3280 CO₂ and 0.0695 H₂O. C=62.0; H=5.3.

C₁₀H₁₀O₄ requires C=61.9; H=5.2 per cent.

Lactone of 2-Hydroxy-4-acetoxy-5-methoxy- β -phenylpropionic Acid.—This substance is obtained by the action of acetic anhydride on either 2:4-dihydroxy-5-methoxy- β -phenylpropionic acid, or the corresponding lactone. It crystallises from methyl alcohol in glistening plates, melting at 135°:

0.1180 gave 0.2644 CO₂ and 0.0570 H₂O. C=61.1; H=5.4.

C₁₂H₁₂O₅ requires C=61.0; H=5.1 per cent.

2:4:5-Trimethoxy- β -phenylpropionic acid was obtained by the action of methyl sulphate and potassium hydroxide on 2:4-dihydroxy-5-methoxy- β -phenylpropionic acid, as in the case of the corresponding 2:4:5-trimethoxycinnamic acid. It crystallises from its aqueous solution in small, glistening needles, containing one molecule of water of crystallisation, and melts at 74—76°. On drying in a vacuum, the water of crystallisation is lost, and the substance then melts at 95—96°:

0.1710,* on heating at 110°, lost 0.0124 H₂O. H₂O=7.2.

0.1604 † gave 0.3520 CO₂ and 0.0970 H₂O. C=59.8; H=6.7.

C₁₂H₁₆O₅·H₂O requires H₂O=7.0 per cent.

C₁₂H₁₆O₅ requires C=60.0; H=6.7 per cent.

Methyl 2:4:5-trimethoxy- β -phenylpropionate was formed on saturating a methyl-alcoholic solution of 2:4:5-trimethoxy- β -phenylpropionic acid with hydrogen chloride. It crystallises from water or methyl alcohol in small, colourless needles, melting at 54°:

0.1312 gave 0.2944 CO₂ and 0.0854 H₂O. C=61.2; H=7.2.

C₁₃H₁₈O₅ requires C=61.4; H=7.1 per cent.

* Air-dried.

† Anhydrous substance.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E C.

CX.—*Reactivity of the Halogens in Organic Compounds. Part VI. The Mechanism of Negative Catalysis.*

By GEORGE SENTER and ALFRED WILLIAM PORTER, F.R.S.

IN the latest paper of this series (this vol., p. 45) the results of an experimental investigation of the rate of reaction between silver nitrate and the esters of bromo-substituted fatty acids were communicated. The kinetics of the reactions of silver nitrate with bromoacetic and bromopropionic acids respectively have now been investigated, and the results are given in the present paper. The nitric acid formed in the course of the reaction retards the change to an even greater extent than in aqueous solution (compare *Trans.*, 1910, **97**, 346). This is to be regarded as an example of negative catalysis, and in the course of the investigation it has been found that the generally accepted method of representing negative catalysis (*Ostwald, Allgemeine Chemie*, II, **2**, 270) is not in accord with the available experimental data. On the basis of the experimental results communicated in the present paper, and also of the data already obtained for the retardation of the hydrolytic decomposition of the bromo-fatty acids by the hydrobromic acid formed in the course of the reaction (*Senter, Trans.*, 1909, **95**, 1827), suggestions for the mathematical representation of negatively catalysed reactions are put forward.

EXPERIMENTAL.

The measurements were carried out as described in the previous paper dealing with the esters (*loc. cit.*). The solutions were warmed separately in the thermostat, and then mixed in a number of small tubes. At definite intervals, the contents of a tube were transferred to a beaker containing a slight excess of *N*/50-ammonium thiocyanate, and the excess of thiocyanate then estimated by means of *N*/50-silver nitrate.

If there were no retarding effect due to the nitric acid, the reactions would be approximately bimolecular. In order to illustrate the magnitude of the retardation, the velocity-coefficients are calculated by the ordinary formula for a bimolecular reaction, and are represented in the tables by k_{bimol} . As in previous papers, the coefficients are referred to a concentration of $1/(12 \times 50)$ mols. per litre, and in order to refer them to a concentration of 1 mol. per litre must be multiplied by 600. The unit of time is one minute

throughout. The majority of the experiments were made at 49.9° ; a few at 26° .

TABLE I.

Temperature 49.9° .

Solvent: Ethyl alcohol. Bromoacetic acid, $N/20$. Silver nitrate, $N/20 \times 0.98$.			Solvent: Methyl alcohol. Bromoacetic acid, $N/20$. Silver nitrate, $N/20 \times 1.05$.		
t (min.).	$a-x$.	$k_{\text{bimol.}} \times 10^4$.	t (min.).	$a-x$.	$k_{\text{bimol.}} \times 10^4$.
0	29.5	—	0	31.4	—
15	28.45	0.83	15	30.2	0.84
45	27.2	0.63	45	28.7	0.65
135	24.4	0.52	135	26.25	0.46
405	19.45	0.43	405	21.95	0.34

Bromopropionic acid, $N/20$. Silver nitrate, $N/20 \times 0.99$.			Bromopropionic acid, $N/20$. Silver nitrate, $N/10 \times 1.04$.		
t (min.).	$a-x$.	$k_{\text{bimol.}} \times 10^4$.	t (min.).	$a-x$.	$k \times 10^4$.
0	29.5	—	0	31.1	—
5	24.9	12.5	5	27.6	9.5
15	20.85	9.4	15	25.2	5.1
45	17.7	5.0	45	22.3	2.8
135	14.0	2.8	135	18.3	1.7

Temperature 26° . Solvent: Ethyl Alcohol.

Bromopropionic acid, $N/20$	$\left. \begin{array}{l} a-x \text{ from } 30.0 \text{ to } 24.0 \text{ c.c. in } \\ 180 \text{ minutes.} \end{array} \right\}$	$k \times 10^4 \text{ from } 1.52 \text{ to } 0.46.$
Silver nitrate, $N/20$		
Bromoacetic acid, $N/10$	$\left. \begin{array}{l} a-x \text{ from } 30.0 \text{ to } 18.0 \text{ c.c. in } \\ 2400 \text{ minutes.} \end{array} \right\}$	$k \times 10^4 \text{ from } 0.051 \text{ to } 0.041.$
Silver nitrate, $N/20$		

Solvent: Methyl Alcohol.

Bromopropionic acid, $N/30$	$\left. \begin{array}{l} a-x \text{ from } 20.0 \text{ to } 18.45 \text{ c.c. } \\ \text{in } 90 \text{ minutes.} \end{array} \right\}$	$k \times 10^4 \text{ from } 1.3 \text{ to } 0.5.$
Silver nitrate, $N/30$		

Apart from the gradual fall in the magnitude of the velocity coefficients, the above results illustrate two important facts. In the first place, the rate of reaction between α -bromopropionic acid and silver nitrate is rather less in methyl and in ethyl alcohol, both at 49.9° and at 26° . In an earlier paper (*loc. cit.*, p. 352) it was shown that the velocity of the same reaction is practically the same in water and in 50 per cent. alcohol, so that it is nearly independent of the nature of the solvent. The esters, on the other hand, react with silver nitrate more rapidly in methyl than in ethyl alcohol (*loc. cit.*, p. 100).

The second point has reference to the magnitude of the temperature-coefficients of the reaction velocity. Calculating from the same stages of the respective reactions, it is seen that the rates of both reactions are increased about nine times by raising the temperature

from 26.0° to 49.9° , so that the average coefficient for 10° is about 2.5. This is exactly the same as for the esters (*loc. cit.*, p. 100).

Before entering on a discussion of the mechanism of the reactions, it is important to find whether any error arises from esterification of the acids while measurements are being made. This would, of course, modify the reaction velocity, as the esters are throughout less active than the corresponding acids. The results of some experiments in ethyl alcohol at 49.9° , in which nitric acid was used as catalytic agent, are given in the accompanying table.

TABLE II.

Bromopropionic acid, $N/10$	}	$k \times 10^4 = 0.033.$
Nitric acid, $N/20$		
Bromoacetic acid, $N/10$	}	$k \times 10^4 = 0.072.$
Nitric acid, $N/20$		

The velocity constants quoted represent the rate of esterification during the first two or three hours—the duration of the experiments. In the later stages of esterification the constants become considerably greater. The data show that esterification does not become appreciable in the comparatively fast reaction between silver nitrate and bromopropionic acid, but may exert some influence on the much slower reaction between silver nitrate and bromoacetic acid. In applying these results to elucidate the nature of negative catalysis, only the measurements with bromopropionic acid are taken into account.

Since the falling off in the magnitude of the velocity constants as the reaction proceeds has been ascribed to the accumulation of nitric acid in the system, it is of interest to find the effect of adding nitric acid at the beginning of the reaction. A solution of the acid in absolute alcohol was therefore prepared by adding to a solution of silver nitrate in alcohol just sufficient of an alcoholic solution of hydrogen chloride to precipitate all the silver. The results of the experiments are given in the accompanying table.

TABLE III.

Bromopropionic acid, $N/20$.			Silver nitrate, $N/20$.		
Nitric acid, $N/40$.			Nitric acid, $N/80$.		
(min.).	$a - x.$	$k \times 10^4$	t (min.).	$a - x.$	$k \times 10^4$
0	29.5	—	0	29.5	—
20	27.85	1.00	10	28.15	1.9
60	25.4	0.92	30	25.2	1.9
120	22.9	0.82	60	23.2	1.5
240	19.2	0.75	120	20.3	1.3

The data show that the retardation due to the nitric acid is, in the first instance, proportional to the amount of the acid added.

The magnitude of the retardation is very striking; *N*/40-nitric acid reduces the speed to about one-fifteenth of its original value. The effect is much greater than for the corresponding reaction in aqueous solution (*loc. cit.*, p. 351), in which circumstances *N*/15-nitric acid reduces the speed to about one-seventh of the original. This is in entire accord with the view as to the mechanism of the reaction advocated in the previous paper, as the difference in the strengths of nitric and of bromopropionic acid is much greater in alcoholic than in aqueous solution (compare Godlewski, *Bull. Acad. Sci. Cracow*, 1904, **6**, 239; Baly, Burke, and Marsden, *Trans.*, 1909, **95**, 1096).

The next point to be taken into consideration is whether the amount of acid formed is equivalent to that of the silver nitrate used up. The matter was investigated by simultaneous titration of the silver nitrate remaining and of the nitric acid formed as the reaction proceeded. For the latter purpose, the reaction mixture was added to an excess of potassium bromide solution to remove the silver nitrate, and the mixture then titrated with *N*/20-sodium hydroxide solution in the usual way. The results of one series of measurements, referred to the same standard of concentration, are given in the accompanying table.

TABLE IV.

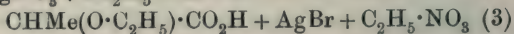
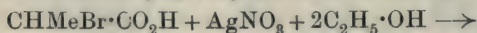
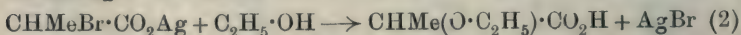
<i>t</i> (min.).	AgNO ₃ used up.	HNO ₃ formed.	Ratio HNO ₃ /AgNO ₃ .
0	0.0	0.0	—
5	4.6	3.0	65 per cent.
15	8.05	5.4	67 „
45	11.8	7.5	63 „
135	15.5	9.3	61 „

The figures show that the amount of nitric acid set free is about two-thirds of that of the silver nitrate used up, and that the ratio remains practically constant throughout the change. The simplest interpretation of these observations is that the silver nitrate is being used up in two simultaneous reactions, in one of which no nitric acid is liberated.

When bromopropionic acid and silver nitrate are mixed, we may assume with certainty that the following equilibrium is immediately established:



In the light of the above results, the two simultaneous reactions:



may then be assumed to occur. In reaction (2) an amount of

nitric acid is liberated equivalent to that of the silver nitrate used up; in reaction (3) no nitric acid is formed. The method of representing the results mathematically is dealt with in the next section on negative catalysis.

Negative Catalysis.

The results communicated in the present paper, and those obtained for the decomposition of the bromo-fatty acids by water, for example, bromopropionic acid, as represented by the equation:



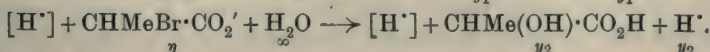
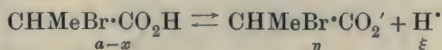
throw considerable light on the question of negative catalysis, especially of negative autocatalysis, a branch of chemical dynamics which has hitherto been very much neglected. The mathematical representation of negative catalysis generally accepted is that given by Ostwald (*loc. cit.*, p. 270). For a unimolecular reaction, the differential equation takes the following form:

$$\frac{dx}{dt} = k_1(a - x) - k_2x(a - x),$$

where the symbols have the usual significance. In the simplest case here dealt with, a would represent the initial concentration of the bromopropionic acid, and x that of the negative catalyst, the hydrobromic acid, formed in the course of the reaction.

It is evident from the form of the above equation that when the ratio k_2/k_1 is sufficiently large, dx/dt becomes zero; in these circumstances, the reaction will come to an end before decomposition is complete, and, further, it will not approach the end-point in an asymptotic manner, as in the great majority of reactions which have been carefully investigated. Now there does not appear to be any experimental evidence of the occurrence of a "false equilibrium" of this nature in a homogeneous system, and it will be evident from what follows that Ostwald's formula is incompatible with the experimental results obtained for negatively catalysed reactions in this and the previous papers of the series.

The method of formulating the hydrolytic decomposition of bromopropionic acid will now be considered on the assumption (compare Senter, *Trans.*, 1909, **95**, 1836) that both the $\text{CHMeBr}\cdot\text{CO}_2'$ ions and the non-ionised acid undergo change. The equations are as follows:



The concentrations of the various substances present at the time t , expressed in the usual way, are given below the respective formulæ. The initial concentration of the acid, as determined by titration (thus including both ionised and non-ionised acid), is represented by a . What is measured in this case is the rate at which the total acidity of the solution increases; the difference between total acidity at any time and initial acidity, which is a measure of the total rate of hydrolytic decomposition, is expressed on the above basis by $y_1 + y_2$. It is, of course, assumed that the establishment of the equilibrium between the acid and its ions is instantaneous.

The equations connecting the different variables are as follows:

$$\frac{\eta\xi}{a-x} = c; \quad \frac{dy_1}{dt} = k_1(a-x); \quad \frac{dy_2}{dt} = k_2\eta$$

$$x = \xi = \eta + y_1 + y_2,$$

as will be evident without further explanation.

The integral of these equations has the following form:

$$- \left[\frac{k_2^2 c}{k_1^2} + a \right] \log_e \left(x + \frac{k_2 c}{k_1} \right) - \frac{(a+c)k_2}{k_1} \log_e (a+x) +$$

$$\left(a + \frac{k_2 c}{k_1} \right) \log_e x = k_2 \left(a + \frac{k_2 c}{k_1} \right) t + \text{constant}.$$

Of the factors of this equation, c , which is proportional to the dissociation constant of bromopropionic acid (assumed to be 0.00108 at 79°), is 0.131; k_1 , the rate of hydrolysis of the non-ionised acid, has already been obtained by measurements in the presence of excess of hydrobromic acid: it amounts to 0.00053 at 79°; a is 11.8; and the only unknown is k_2 , the velocity coefficient for the reaction between $\text{CHMeBr} \cdot \text{CO}_2'$ ions and water.

The most severe test of the applicability of the equation is to use it for the case in which no hydrobromic acid is added at the commencement of the reaction (table V, columns 1 and 2). The last column contains the values of the velocity coefficient calculated for a reaction of the first order—as is to be anticipated, they diminish rapidly during the reaction.

TABLE V.

t .	$C_t = a - (y_1 + y_2)$.	$y_1 + y_2$ (obs.).	$y_1 + y_2$ (calc.).	x .	$k_{\text{unimol.}}$
0	11.8	0.0	0.0	1.18	—
120	8.8	3.0	2.85	3.2	0.0024
240	7.3	4.5	4.4	4.6	0.0019
360	6.3	5.5	5.45	5.6	0.0015
1380	2.2	9.6	9.5	9.5	0.0010

It has now been found that the equation is almost exactly satisfied by putting $k_2 = 0.030$. One test is that when the left

hand side of the equation is plotted against t , a straight line is obtained, as the equation requires, and, further, the slope of the line agrees with the value $k_2(a + ck_2/k_1)$. Another test is to find by successive approximations the values of x which satisfy it for different values of t , and from these calculating the values of $y_1 + y_2$ by means of the equations $\eta x/(a - x) = c$ and $y_1 + y_2 = x - \eta$ connecting the variables. The observed and calculated values of $y_1 + y_2$ are given in the third and fourth columns of the table, and it will be seen that the agreement is excellent. The velocity coefficient, k_2 , of the hydrolysis of the $\text{CH}_3\cdot\text{CHBr}\cdot\text{CO}_2'$ ion can also be obtained entirely independently from the rate of hydrolysis of sodium bromopropionate by water. The value thus obtained is 0.035 (*loc. cit.*, p. 1836), which, considering the slight uncertainty as regards the temperature-coefficient of hydrolysis, is in very good agreement with the above value, 0.030. The simple assumptions made in deducing the above formula are therefore justified, and the alternative suggestion of Bodenstein (*Zeitsch. Elektrochem.*, 1909, 15, 403) as to the mechanism of these reactions does not apply.

We now come to the reaction between silver nitrate and bromopropionic acid in alcoholic solution. The first stage in this case is undoubtedly the instantaneous establishment of the equilibrium:



As regards the further progress of the reaction, different assumptions might be made. Without going into the matter fully, we may assume, on the basis of the simpler reaction just considered, that the velocity is proportional to the concentrations of the silver nitrate and acid respectively, and inversely proportional to the nitric acid concentration at the time t . Further, since in alcoholic solution nitric acid is a very much stronger acid than α -bromopropionic acid (p. 1052), there will be no appreciable error in taking its concentration at any time, t , as that liberated in the reaction ($\frac{2}{3}x$, compare p. 1052). The differential equation on this basis is therefore:

$$dx/dt = k(a - x)^2/\frac{2}{3}x,$$

which, on integration, and taking $x = 0$ when $t = 0$, becomes:

$$\frac{x}{a - x} - \log_e \frac{a}{a - x} = \frac{3kt}{2}.$$

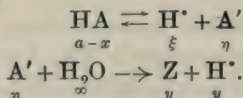
The results of the calculation of the experimental data according to this equation are given in table VI.

TABLE VI.

t	0	5	15	45	135
$a-x$	29.5	24.9	21.45	17.7	14.0
k	—	0.0021	0.0024	0.0023	0.0017

The coefficients for the greater part of the reaction are nearly constant, and proved the applicability of the formula. The fall after one hundred and thirty-five minutes is probably due to some secondary reaction, for example, to esterification of the bromopropionic acid. The equation was further tested by applying it to the case where nitric acid was added at the beginning of the reaction. The coefficient in this case was 0.0021, in good agreement with the above results.

General Considerations.—The reaction between bromopropionic acid and water is complicated by the fact that both the ions and the non-ionised acid undergo decomposition. A simpler case would be that in which only the ion undergoes hydrolysis. Representing the general formula of a monobasic acid by HA, we have the following equations:



As before, $\eta\xi/(a-x)=c$ and $x=\xi=y+\eta$,

therefore: $\frac{dy}{dt} = k\eta = kc(a-x)/\xi$,

that is, the rate of the reaction (the rate at which η is formed) is inversely proportional to ξ , the concentration of the negative catalyst.

If the acid is only slightly ionised, we can put $dx/dt=dy/dt$ without serious error, and the equation can then readily be integrated. If, on the other hand, the degree of dissociation is not small, it will in general be possible to integrate the equation on the basis of some relationship between the different factors found experimentally.

It appears justifiable to extend these considerations to the phenomenon of negative catalysis in general. It has been shown that the representation of this type of catalysis as a difference between two factors (p. 1053) is not generally applicable. An empirical equation which in certain cases at least is in accordance with the experimental facts, may be based on the assumption that the rate of reaction is proportional to the respective concentrations of the reacting substances, and inversely proportional to the concentration of the negative catalyst. The only satisfactory case met with, apart from the foregoing, in which a formula of this type has been

used, is the hydrolytic decomposition of bromosuccinic acid by water, investigated by Müller (*Zeitsch. physikal. Chem.*, 1902, **41**, 483), but the author has not drawn from his observations any general conclusions regarding negative catalysis.

In the ideal type of positive catalysis, it is assumed that the catalyst does not alter the free energy of the reacting substances. In many cases of positive catalysis, however, the free energy is undoubtedly altered, although perhaps only to a slight extent. In the examples of negative catalysis quoted in the present paper, and perhaps in all cases of negative catalysis, the free energy of the reacting substances is diminished by the presence of the catalyst. According to the view here advocated, a negative catalyst acts by diminishing the active mass of one or more of the reacting substances. The method used in obtaining accurate mathematical formulæ on this basis will be evident from the first example quoted in the present paper (p. 1053).

Catalytic Action of Colloidal Silver Bromide.

In a previous paper it has been shown that freshly formed silver bromide has a powerful catalytic effect on the reactions between silver salts and organic halogen compounds in aqueous solution, and it was suggested that the effect might be due to the silver bromide in colloidal solution. Direct evidence has now been obtained on this point by using gelatin as a protective colloid—in this way the coagulation of the silver bromide is entirely prevented. In the following table are given the results of two parallel experiments, the only difference being that one solution contained 0.25 per cent of gelatin.

TABLE VII.

Bromoacetic acid, <i>N</i> /20. Gelatin, 0.25 per cent.			Silver nitrate, <i>N</i> /20. No gelatin.		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	30.0	—	0	30.0	—
30	27.9	0.0025	30	28.7	0.0015
60	25.45	0.0032	60	27.6	0.0013
120	20.55	0.0040	120	25.2	0.0012
240	14.1	0.0038	240	21.25	0.0015
360	10.9	0.0024	360	18.75	0.0011

The results show very clearly the increase in the velocity coefficients when gelatin is present. The effect appears to depend on the gelatin concentration, as the reaction was considerably slower when only one-third of the above proportion was used. In this case, however, the silver bromide coagulated to some extent

towards the end of the reaction. The matter is being further investigated.

Summary of Results.

The kinetics of the reactions of silver nitrate with bromoacetic and α -bromopropionic acids respectively in absolute alcohol have been measured at 49.9° . The reactions are retarded by nitric acid to an even greater extent than in aqueous solution. A formula which represents the results fairly satisfactorily is given.

A formula which represents accurately the decomposition of bromopropionic acid by water has been derived on the assumption that both the anions and the non-ionised acid react with water.

It is shown that the usual formula which represents negative catalysis as a difference between two factors is not in accordance with the available experimental data. An empirical formula, based on the assumption that the rate of reaction is inversely proportional to the concentration of the negative catalyst, is shown to represent the experimental results very closely. The mode in which accurate formulæ representing negative catalysis may be derived is indicated, and the connexion between the accurate and empirical formulæ pointed out.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed most of the expense of this investigation.

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CXI.—*The Relation of Position Isomerism to Optical Activity. Part IX. The Rotation of the Menthyl Esters of the Isomeric Fluoro- and Iodobenzoic Acids and of the Halogen Derivatives of the Fatty Acids.*

By JULIUS BEREND COHEN.

IN a former paper by Cohen and Dudley (Trans., 1910, **97**, 1733) the apparently anomalous optical relation of the ortho-, meta-, and para-iodobenzoic esters was referred to, and, in view of the marked effect of temperature on the alkyloxy-esters to which attention was drawn (*loc. cit.*), it was decided to re-investigate the rotation of

these three compounds at higher temperatures. Fresh specimens have now been prepared and examined, as well as the three isomeric menthyl fluorobenzoates and a number of halogen esters of the aliphatic series.

Iodobenzoic Esters.—Table I gives the physical constants of the iodobenzoic esters. The figures in brackets are the former numbers, which are higher in the case of the ortho- and meta-compounds and lower in that of the para-compound. The accuracy of the present observations has been confirmed by repeating the preparations with different specimens of acid and menthol. Thus, the following polarimeter readings were obtained with (I), an ester prepared from *o*-iodobenzoic acid, from anthranilic acid, and a specimen of menthol in large crystals supplied by a local dealer, and (II), an ester made from Kahlbaum's specimens of *o*-iodobenzoic acid and menthol in small crystals:

	I.	II.
α_D^{20}	-25.52	-25.55
α_D^{100}	24.11	24.14

Two specimens of the para-ester were made in a similar way from (I), an acid prepared by myself and Kahlbaum's menthol, and (II), an acid obtained from Kahlbaum, and menthol in the large crystals referred to:

	I.	II.
α_D^{20}	-25.13	-25.12

TABLE I.

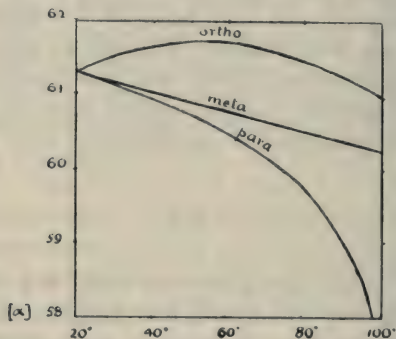
<i>t</i> .	Ortho-ester.			Meta-ester.			Para-ester.		
	<i>d t</i> /4.	$[\alpha]_D^t$.	$[M]_D^t$.	<i>d t</i> /4.	$[\alpha]_D^t$.	$[M]_D^t$.	<i>d t</i> /4.	$[\alpha]_D^t$.	$[M]_D^t$.
20°	1.373	-61.5 (62.5)	-237 (241)	1.366	-61.4 (63.7)	-237.0 (246)	1.353	-61.5 (60.7)	-237.0 (234)
40	1.356	61.6	238	1.349	61.2	236.0	1.335	60.9	235.5
60	1.340	61.8	239	1.331	60.9	235.5	1.309	60.8	235.0
80	1.321	61.6	238	1.312	60.8	235.0	1.298	59.9	231.5
100	1.303	61.2	236	1.295	60.4	233.5	1.281	58.0	224.0

The temperature curves for the specific rotations, when smoothed out, have the general contours shown in the diagram on p. 1060.

At 20° the three isomerides have the same rotation. Rise of temperature produces a slight increase and then a slight decrease in the rotation of the ortho-compound, but the changes are insignificant. In the case of the meta-compound there is a gradual and steady diminution in rotation, whilst the para-compound exhibits a rapid lowering of rotation at the higher temperatures. Consequently, the relation of the ortho- and para-isomerides at 100° is the reverse of that of the corresponding halogen isomerides at 20°, although the actual differences are much smaller in the present case

(see table III below). This result is the more remarkable seeing that the substitution of hydrogen by iodine in the aliphatic menthyl esters, to be presently described, produces a greater effect in lowering the rotation both at 20° and 100° than that of either chlorine or bromine.

Fluorobenzoic Esters.—The three isomeric fluorobenzoic acids were prepared by oxidation of the corresponding fluorotoluenes, specimens of which were very kindly placed at my disposal by



Temperature-rotation curves of the isomeric menthyl iodobenzoates.

Professor Holleman, to whom I desire to express my sincere thanks. Table II gives the constants for the three esters at 20° and 100° .

TABLE II.

Menthyl ester.	$d\ 20/4$.	$d\ 100/4$.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	$[\alpha]_D^{100}$.	$[M]_D^{100}$.
Ortho-	1.055	0.9972	-70.0	-194.5	-68.0	-188.5
Meta-.....	1.050	0.9922	84.8	236.0	82.5	229.0
Para-	1.052	0.9933	86.1	239.0	82.8	230.0

A comparison between the above isomerides and the corresponding chlorine and bromine compounds shows a precisely similar relationship. There is a marked diminution in the case of the ortho-compound, which is somewhat less than that of the chlorine derivative, whereas the meta- and para-compounds correspond closely with the unsubstituted benzoic ester. Table III exhibits these relationships.

TABLE III.

Menthyl ether.	$[M]_D^{20}$.			
	F.	Cl.	Br.	I.
Ortho-	-194.5	-195	-205	-237
Meta-	236.0	237	239	237
Para-.....	239.0	237	239	237

Benzoic ester, $[M]_D^{20} = 239$.

It should be pointed out that the error on the actual reading is multiplied about ten times in the molecular rotation, so that the observed differences in the meta- and para-compounds are only a few units in the first decimal place.

Menthyl Esters of the Halogen Fatty Acids.—Table IV gives a summary of the constants of the esters examined.*

TABLE IV.

Menthyl ester.	d 20/4.	d 100/4.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	$[\alpha]_D^{100}$.	$[M]_D^{100}$.
Acetic†	0.9244	0.8626	-77.6	-153.7	-76.5	-151.5
Chloroacetic	1.041	0.9760	75.1	174.6	72.8	169.7
Dichloroacetic	1.114	1.044	62.8	167.8	61.1	163.2
Trichloroacetic	1.181	1.110	58.5	176.5	58.8	177.3
Bromoacetic	1.217	1.123	61.3	169.7	60.7	168.3
Iodoacetic	1.376	1.299	49.0	158.7	47.6	154.3
Nitroacetic	1.128	—	66.9	162.7	—	—
Propionic (T).....	—	—	75.5	160.8	—	—
α -Chloropropionic	1.011	0.9475	62.9	155.2	62.1	153.1
β - "	1.025	0.9625	62.6	154.3	58.8	145.0
α -Bromopropionic	1.180	0.109	54.4	158.4	53.4	155.2
α -Iodopropionic	1.324	1.247	42.8	144.9	42.0	142.2
Phenylacetic (C. and D.)...	1.002	0.9400	68.7	188.2	65.5	179.6
Phenylchloroacetic	1.064	1.003	67.2	207.2	61.7	190.5
Phenylbromoacetic	1.201	1.140	57.2	202.2	52.6	185.7

(T.) = Tschugaeff; (C. and D.) = Cohen and Dudley.

If we take as our basis for comparison the "specific rotations," that is, the rotations produced by equal masses, the substances arrange themselves in a comparatively simple order, the unsubstituted ester giving the highest rotation, and the increase in number or mass of the halogen atoms causing a successive diminution in the amount of deviation. It is obvious that a comparison of equal masses can lead to no satisfactory generalisation as to molecular relations, and unless there is reason to suppose that association modifies the results, which does not appear to be the case here, the "molecular rotation," or the rotation produced by equal numbers of molecules, is the only satisfactory basis. If this is granted, we

* When the above observations were made I was unaware that Tschugaeff had already determined the rotatory power of some of the halogen esters given in the table (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606). The constants given by Tschugaeff do not differ materially from my own, and are as follows:

	$[\alpha]_D^{20}$.	$[M]_D^{20}$.		$[\alpha]_D^{20}$.	$[M]_D^{20}$.
Menthyl chloroacetate	-73.86	-171.2	Menthyl bromoacetate	-60.95	-168.8
„ dichloroacetate	63.56	168.7	„ α -bromo-		
„ trichloroacetate	59.05	176.8	propionate ..	54.52	158.6

† Tschugaeff found the specific rotation of menthyl acetate at 20° to be -79.42°, which is almost identical with that of menthyl formate, -79.52°, whilst that of menthyl propionate is given as -75.5°. I have carefully redetermined the value of menthyl acetate, which I find much lower, being almost the mean of the other two esters.

shall have to confine our attention to the fifth and seventh columns of the table. An examination of these numbers leads to no simple generalisation, for the effect of substitution in one series appears to contradict the results in another. For example, the introduction of chlorine and bromine into acetic and phenylacetic acid raises the rotation; but this is the reverse of what occurs in the case of propionic acid. The only single observation which recurs in the acetic and propionic ester series is the minimum rotation of the iodine derivative; but here again its relation to the unsubstituted ester is very different in the two series. The only result of any significance that can be drawn from the above set of observations is that among the halogens the atom of largest mass produces the greatest effect, a result which is precisely the reverse of that manifested in nuclear substitution.

EXPERIMENTAL.

The iodobenzoic esters were prepared in the manner described by Cohen and Raper (Trans., 1904, **85**, 1272), and apart from the slight differences in rotation already recorded, no material difference in physical properties of the esters or intermediate products has been observed.

Menthyl Fluorobenzoates.—The three isomeric acids and acid chlorides were prepared from the fluorotoluenes by the method described by Holleman and Slothouwer (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, p. 497), using a strong solution of permanganate, as recommended by Ullmann. About 20 grams of fluorotoluene were employed in each case, and heated in the water-bath with 50 grams of permanganate dissolved in 1 litre of water. About half the material was oxidised, and the unaltered portion recovered by distillation in steam. The filtered liquid, on acidifying with sulphuric acid and concentrating, gave a pure product in each case. The acid was converted into the acid chloride by heating with the calculated quantity of phosphorus pentachloride on the water-bath until the evolution of hydrogen chloride had nearly ceased. The phosphoryl chloride was removed by distillation on the water-bath under diminished pressure. Each of the acid chlorides after distillation under diminished pressure was heated with the equivalent amount of menthol in the oil-bath for several hours at about 120–130° until the reaction was complete. The reaction in the case of the ortho-compound began at about 90°, in that of the meta- at 100°, and in that of the para- at 103°. Steric hindrance does not apparently come into play. The esters were purified by distilling in steam to remove free menthol, and shaken with sodium carbonate to remove free acid, then extracted with

ether, dehydrated, and finally distilled under reduced pressure. The esters are colourless, rather viscid liquids, with a very faint, fruity odour. The para-compound solidified on keeping in colourless needles, melting at 36° .

The following table contains a summary of the constants of the above three esters and intermediate products:

	Fluorobenzoic acids.	Fluorobenzoyl chloride.		Menthyl fluorobenzoate.	
	M. p.	B. p.	Pressure.	B. p.	Pressure.
Ortho-	124°	99°	13 mm.	$181-185^{\circ}$	12 mm.
Meta-	123	91	18 "	186	15 "
Para-	182	104	38 "	$188-189$	20 "

The following are the polarimeter readings of the undistilled (I) and the distilled esters (II)*:

	Ortho-ester.		Meta-ester.		Para-ester.	
	α^{20} .	α^{100} .	α^{20} .	α^{100} .	α^{20} .	α^{100} .
I.	22.31	20.46	26.93	24.72	27.36	24.85
II.	22.37	20.55	26.88	24.62	27.28	24.85

Neither in the above menthyl esters nor in any other ester described in the present paper has any indication been given of racemisation on distillation under reduced pressure.

Menthyl monochloroacetate was prepared by heating monochloroacetyl chloride with rather less than the calculated amount of menthol until hydrogen chloride ceased to be evolved; the liquid was then shaken with sodium carbonate to decompose any excess of acid chloride, the ester extracted with ether, the ethereal solution dehydrated with calcium chloride, and distilled. The ester, which is colourless, boils at $136-137^{\circ}/12$ mm., and crystallises in colourless needles, melting at $37-38^{\circ}$. The liquid is unchanged by distillation under diminished pressure, the readings after one and three distillations being almost identical. The following readings were obtained with a 0.302-dcm. tube, which was used throughout these determinations:

	One distillation.	Three distillations.
α^{20}	-23.64	-23.62
α^{100}	21.50	21.47

The substance has the property of remaining supercooled in a remarkable degree in the complete absence of the solid phase; for after being first prepared it continued in a liquid condition at the laboratory temperature for about a week, and most of the physical constants were determined without difficulty. At the end of this time the substance suddenly solidified in one of the vessels containing it, and very shortly afterwards it was found to have solidified

* In this and other cases the final results are calculated on the mean of the two sets of readings.

in all which were open to the air. It was then impossible to keep it liquid at the ordinary temperature, even for a few minutes, the atmosphere being probably infected with solid particles. The final density determinations at 20° had consequently to be carried out in another room.

Menthyl Monobromoacetate.—The ester was prepared from bromoacetyl bromide as described above. It boiled constantly at 146—147°/12 mm., and gave the following polarimeter readings:

$$\alpha^{20} - 22.53; \quad \alpha^{100} - 20.60.$$

Menthyl iodoacetate was prepared from the previous ester. Twenty-five grams of bromoacetic ester, 25 grams of potassium iodide, and 50 c.c. of methyl alcohol were boiled on the water-bath under reflux for several hours. Water was added, and sulphur dioxide passed into the solution to remove a little free iodine. The ester was extracted with ether, shaken with sodium carbonate solution, and dehydrated. The ester is a colourless liquid, which distils at 161—162°/12 mm. A little free iodine which appeared at the end of the distillation was removed by shaking with mercury, and filtering; the yield was 25 grams. The following readings were obtained with two different specimens:

	I.	II.
α^{20}	- 20.41	- 20.30
α^{100}	18.64	18.73

Menthyl dichloroacetate was prepared like the monochloroacetate from dichloroacetyl chloride and menthol. Fifteen grams of the acid chloride and 14 grams of menthol gave 21 grams of ester, boiling at 173—174°/37 mm. The readings were:

$$\alpha^{20} - 21.14; \quad \alpha^{100} - 19.28.$$

Menthyl trichloroacetate was prepared like the monochloroacetate, and distilled at 149°/10 mm. It solidified on cooling in long, colourless needles, melting at 23°. The readings were:

$$\alpha^{20} - 20.88; \quad \alpha^{100} - 19.71.$$

Menthyl nitroacetate was obtained by heating in the oil-bath to 120° for six hours menthyl iodoacetate and an excess of dry silver nitrite in powder. The product was extracted with ether, dehydrated, and the ether removed. The liquid has a yellow colour and a faint aromatic odour, and distils at about 170°/12 mm. with partial decomposition. The rotation of the undistilled liquid was determined as follows:

$$\alpha^{20} - 22.81.$$

0.1975 gave 9.9 c.c. N_2 (moist) at 15° and 756 mm. $N = 5.89$.

$C_{12}H_{21}O_4N$ requires $N = 5.75$ per cent.

Menthyl α -chloropropionate was obtained from the acid chloride

as previously described. It is a colourless liquid, which distils at $139^{\circ}/12$ mm., and gave the following readings:

$$\alpha^{20} -19.23; \alpha^{100} -17.78.$$

Menthyl β -chloropropionate, prepared as above, is a colourless liquid, with a faint, fruity odour, and distils at $151^{\circ}/20$ mm. It gave the following reading:

$$\alpha^{20} -19.38; \alpha^{100} -17.10.$$

Menthyl α -bromopropionate was prepared from the acid bromide. It distils at 147 — $149^{\circ}/12$ mm. The rotations after one and two distillations were practically unchanged:

	One distillation.	Two distillations.
α^{20}	-19.47	-19.23
α^{100}	17.86	17.86

Menthyl α -iodopropionate was prepared by heating 19 grams of the above bromopropionic ester with 15 grams of potassium iodide for one and a-half days. The yield of crude product was 21 grams. It distilled without decomposition at 161 — $162^{\circ}/12$ mm., and solidified on cooling in colourless crystals, melting at 49° , which turned yellow on exposure to light. The undistilled (I) and distilled (II) specimens gave the following results:

	I.	II.
α^{20}	-17.31	-17.00
α^{100}	16.00	15.83

Menthyl Phenylchloroacetate.—The acid chloride was obtained by Walden's method (*Ber.*, 1895, **28**, 1293), and boiled at $120^{\circ}/15$ mm. It was heated with the calculated quantity of menthol in the oil-bath to 120° for several hours. The product was an amber-coloured liquid, with a faint aromatic odour, which distilled at 200 — $201^{\circ}/12$ mm. as a colourless oil. The rotation was determined (I) before and (II) after distillation:

	I.	II.
α^{20}	-21.61	-21.53
α^{100}	18.73	18.70

Menthyl Phenylbromoacetate.—The acid bromide was prepared by Walden's method (*loc. cit.*). It distilled at 138 — $140^{\circ}/15$ mm. as a nearly colourless liquid. Twenty grams of mandelic acid gave 15 grams of pure acid bromide. The acid bromide was heated with menthol to 105° for two hours, and the ester purified in the usual way. It distilled at $225^{\circ}/22$ mm., and, on cooling, formed crystals, melting at 80° . The yield was 19 grams. The readings after distillation were:

$$\alpha^{20} -20.78; \alpha^{100} -18.11.$$

An attempt to prepare the iodine derivative by heating to 140° a mixture of phenylbromoacetic ester and potassium iodide failed, the product being mainly unchanged bromine compound.

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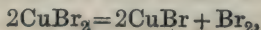
CXII.—*The Dissociation of Cupric Bromide and Some Forms of Glass Manometer.*

By COLIN GYRTH JACKSON.

THE use of a glass pressure gauge for the measurement of pressures of vapours which attack mercury, or for measurements in which the experiment requires the manometer to be at a high temperature, was introduced by Ladenburg (*Ber. Deut. physikal. Ges.*, 1906, **8**, 20). For the statical determination of vapour pressures of many pure substances and dilute solutions, and of chemical equilibria, a glass manometer is almost indispensable. Various forms have been described by Ladenburg (*loc. cit.*), Johnson (*Zeitsch. physikal. Chem.*, 1908, **61**, 457), Bodenstein (*ibid.*, 1909, **69**, 26), and Gibson (*Diss.*, Breslau, 1911). Some of these were tried, and found to have disadvantages, and, as a consequence, attempts at improvement were made, and finally three workable modifications constructed (figure: 1, 2, 3).

These consist of one or more thin plano-convex or concavo-convex bulbs about $1\frac{1}{2}$ to 2 cm. in diameter, which change their shape when pressure is applied inside or out. The extent of this elastic deformation is measured by the angular movement of a fine glass pointer, which forms a continuation of the bulb, and is drawn out in the blowing operation.

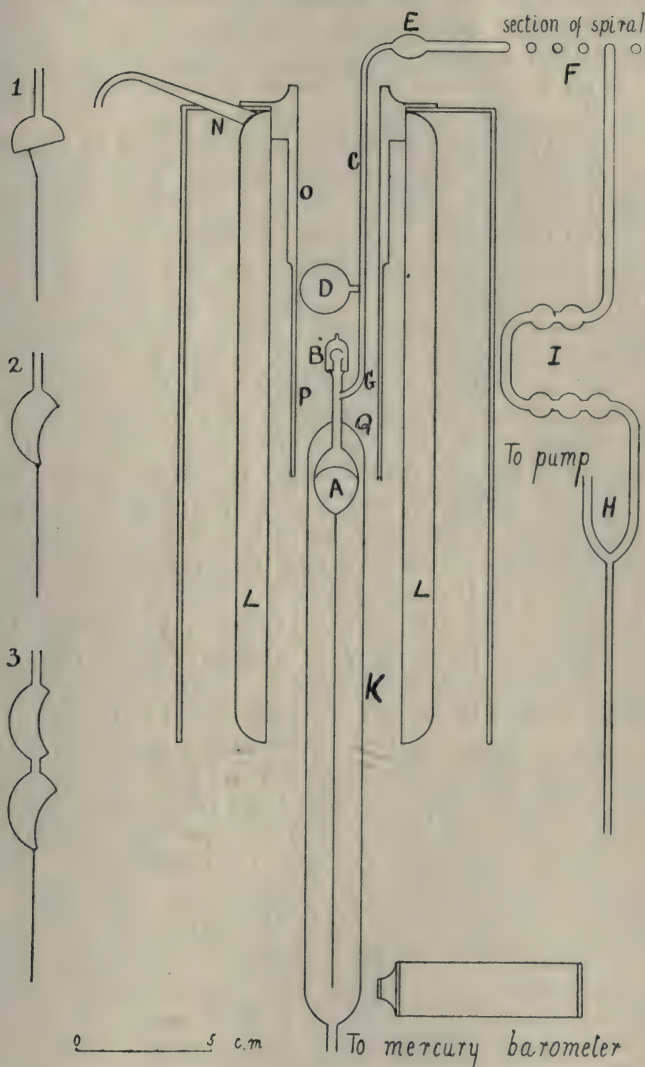
Among the cases of chemical equilibria for the study of which such a manometer is suitable, are many in which only one of the reacting substances has a considerable vapour pressure, the magnitude of which at a given temperature is independent of the amounts of the other substances as long as they are all present and do not dissolve in each other. In such a case, a knowledge of the vapour pressure suffices for the calculation of the affinity of the reaction. The dissociation of cupric bromide:



was chosen for investigation, and the method adopted was to raise the substance to various known temperatures in a small chamber connected with the inside of the glass manometer bulb, and balance

the pressure exerted by the bromine by an equal measured air pressure on the outside.

Part of the apparatus is shown in the figure. In making a deter-



mination, powdered cupric bromide was placed in the vaporisation chamber *B* (the oven being removed), and the whole apparatus, on both sides of the manometer *A*, exhausted. The copper bromide and the neighbouring parts of the apparatus were then heated, so

that bromine was freely evolved, and volatile impurities, such as air, water, and hydrogen bromide, were driven out and the tube *C* sealed at *G*, the spiral *F* providing the necessary play.

The rush of bromine was arrested by the mercury trap *H* until it was absorbed by mercury dew on the walls of the bulbs *I*, and so prevented from reaching the pump. The trap also prevented any traces of air or moisture which leaked through various taps from reaching the copper bromide when left overnight.

The tube *D* contained phosphoric oxide sublimed in a current of oxygen passed over hot platinised asbestos; *E* is a joint blown between the Jena-glass manometer, etc., and ordinary glass tubing; it held well throughout, and could be heated in a smoky flame. The passages connecting the manometer and the floor of the vaporisation chamber with the pump were nowhere less than 1.5 mm. diameter, and were mostly wider. After sealing off at *G*, and removing, for convenience, *C*, *D*, *E*, and *F*, the oven was let down over the vaporisation chamber and the manometer, the latter being enclosed in, and supported by, a wide glass tube, which will be referred to as the "manometer tube" (*K*). The oven consisted of a double-walled cylinder of brazed copper, shielded by an asbestos jacket *M*, and heated by a ring burner supplied with gas through a regulator connected with the air-tight space between the cylinder walls by a long, thin copper tube, which was heated at *N*, where it emerged from the asbestos jacket, to prevent local cooling. Inside *L* another cylinder, the upper half *O* made of asbestos, the lower *P* of copper, reached down to the shoulder *Q* of the manometer tube *K*, round which asbestos wool was closely packed to support vertically about forty rods of thick copper wire 55 mm. long (not shown in the figure), so that they surrounded the vaporisation chamber *B* and extended about 20 mm. above and below it. By this means the temperature gradient in a vertical direction was decreased to 0.05° per cm. The manometer itself was below this region, and from 10° to 20° hotter. The oven was closed above and below with asbestos wool. The pointer of the manometer extended downwards in the manometer tube to about 12 cm. below the oven, its tip *R* being horizontal, and ending in a fine point, which was observed with an electrometer microscope. Alterations of zero due to relative shift of manometer and microscope were provided against by reading in the same way the position of a scratch on the glass wall of the manometer tube close to the pointer, although not in the same focal plane, the microscope having a racking motion sufficiently free from shake for the purpose. The pointer was about 20 cm. long, and the tip moved horizontally 0.1 mm., that is, five divisions on the eyepiece scale

for a difference of pressure of 1 mm. of mercury, and the manometer withstood a pressure of 150 mm. without alteration of zero. Another one was five times as sensitive. The zero of these manometers is not affected by slow changes of temperature if the latter does not exceed 300° . The oven was supported by a large retort-stand fixed on a wooden tripod fitted with levelling screws, and the rest of the apparatus was fastened to a wooden frame hung against a wall.

For measuring the temperature, two iron-constantan junctions were fixed on opposite sides of the vaporisation chamber. The wires, insulated by capillary glass tubes and beads, led downwards through the hotter parts of the oven to the cold junctions in a Dewar vessel containing ice. The copper leads were connected with a millivoltmeter, and as the scale corresponded only with about 140° , whilst the temperature to be measured ranged from 150° to 300° , the current from the couple was partly compensated* by being made to circulate against the opposing *E.M.F.* of a shunt from a circuit carrying a constant current of from 0.3 to 0.9 amperes, supplied by a large accumulator, and adjusted so that the reading on a sensitive amperemeter in circuit was constant. By means of a commutator the effect on the millivoltmeter of the shunted current alone could also be read. This arrangement was calibrated before and after use with standard thermometers, the error in temperature being probably not more than 0.5° .

At a series of temperatures, which were kept constant within $\pm 0.05^{\circ}$ for half an hour or more, the air pressure outside the manometer bulb was adjusted equal to that of the bromine inside, and measured on a bright steel scale as the difference of levels in a wide, well-boiled-out mercury barometer.

The oven was then removed, and the apparatus opened by breaking with pliers the short capillary at the top of the vaporisation chamber *B*, inside a thin-walled evacuated rubber tube, which was stuffed with cotton-wool to prevent collapsing, and slipped over *B*, the other end being connected with the manometer tube. Inside and outside being thus brought into communication, dry air was admitted, and connexion with the pump re-made; the heating under diminished pressure was then repeated, the pump sealed off, and a further series of pressure readings taken. Successive determinations with widely differing proportions of cuprous and cupric bromide gave identical vapour pressure curves. At low temperatures decomposition was much more rapid than combination, and only above about 250° was equilibrium attained in convenient time for measurement in the process of cooling. From this cause several

* I am indebted to Dr. O. Sackur for suggesting this.

attempts to prepare copper bromide in the dry way from purified bromine and copper were not successful, and a good specimen of Kahlbaum's was used without further purification. It was tested repeatedly for chlorine by the chromyl chloride test, but none was found.

In order further to test its purity and suitability for the experiment, it was heated under the microscope between glass slips slid into a recess in a bundle of copper strips, which were rivetted together, covered with asbestos, and pierced with a hole to afford a view through the glass, the temperature being measured by a thermo-electric junction fixed at the edge of the field of view. The slightly moist appearance vanished below 200° , and a few minute black specks were observed; these remained unchanged on further heating and cooling, and were taken to be copper oxide formed from the interaction of water and cupric bromide, which is hygroscopic. At slightly higher temperatures, greenish-white cuprous bromide appeared in patches, and bromine was given off. The cuprous bromide remained throughout very sharply defined, and seemed not to form a solid solution with the cupric bromide. Sometimes crystals, or agglomerations of several, gave off bromine with a little explosion, scattering particles of solid, and this was also observed on a larger scale. Only when heated quickly in a comparatively large vacuous space, or in a current of gas, did the solid appear to sublime, the product being always greenish-white, and it is assumed that such apparent sublimates were blown over with bromine vapour, and that the pressure measured was essentially that of bromine. The cuprous bromide alone had no measurable vapour pressure at 300° .

Dissociation Pressure of Cupric Bromide.

Series I.

Temperature.	Pressure ; mm. of mercury.		Temperature.	Pressure ; mm. of mercury.	
	Observed.	Calculated.		Observed.	Calculated.
166.0°	3.1	3.0	239.0	118.0	116.5
172.0	3.8	4.2	250.0	186.0	185.0
180.5	6.8	6.5	259.4	272.0	270.5
203.5	22.0	22.5	266.3	353.5	355.0
213.0	36.0	35.8	268.2	381.5	382.0
222.8	55.4	56.6	280.2	597.0	600.0
232.3	85.0	87.0	281.0	614.5	616.0

Series II.

198.3	17.0	17.4	247.5	166.0	166.5
212.5	35.7	35.0	264.3	322.0	328.5
229.5	80.0	73.5	274.8	484.5	491.0
244.3	152.0	146.0	279.1	576.5	577.0
247.0	164.5	163.5			

The results of two series of measurements are recorded in the table, temperatures in the first column and observed pressures in the second. The third column contains the pressures calculated from the equation:

$$\ln \frac{p_2}{p_1} = - \frac{Q(T_1 - T_2)}{RT_1 T_2} \quad . \quad . \quad . \quad . \quad . \quad (1),$$

which is obtained by integrating:

$$\frac{d \ln p}{dT} = - \frac{Q}{RT^2}$$

on the assumption that Q , the heat of reaction, is constant between the absolute temperatures T_1 and T_2 .

In order to ascertain whether Q could be taken as constant, and, if so, to find a pair of mean values of temperature and pressure from which to calculate the heat change, the following method was adopted.

On a system of co-ordinates, $T \log p$ was plotted as a function of T , and the points were found to lie approximately on a straight line. Values of T and $\log p$ were taken from this line and inserted in equation (1), giving $Q = 22,400$ calories; from Q and the value for the pressure at $T = 550^\circ$ abs., the pressure at all the experimental temperatures was calculated, and is given in the third column of the table. It will be seen that the calculated and observed pressures agree satisfactorily considering that the percentage accuracy attainable is less in the measurement of the lower than of the higher pressures.

In the foregoing account three varieties of glass manometer have been described, values of the dissociation pressure of cupric bromide at a series of temperatures recorded, and their connexion shown to be adequately represented by an equation involving the constancy of the heat of dissociation, the applicability of the simple gas laws to bromine under the conditions of the experiment, and the first and second laws of thermodynamics.

The work was done at the suggestion of the late Prof. Abegg, and partly under his direction, and I have also to thank Dr. O. Sackur for advice and criticism, and Dr. H. M. Dawson for subsequent criticism.

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CXIII.—*The Determination of the Density of Liquids.*

By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

THE object of this investigation was to find the conditions under which a density determination accurate to ± 5 units in the sixth decimal place may be made with simple precautions using about 25 c.c. of liquid, as in many cases the larger amount required for the accurate pycnometer devised by Bousfield (Trans., 1908, **93**, 679) is not available. The practical details of the determination of liquid densities have been discussed by Manley (*Proc. Roy. Soc. Edin.*, 1902, **24**, 356), and the importance of various corrections by Wade and Merriman (Trans., 1909, **95**, 2174).

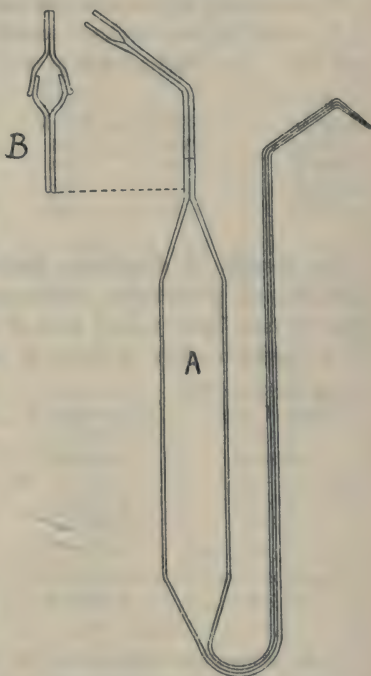
Pycnometers of the forms shown in the figure were made from test-tube glass; the form *A* was used at 18° ; the form *B*, in which there is a bulb to allow the liquid to expand, at 10° and 0° . The cap in the latter form should be ground on outside; otherwise it is difficult to free the ground joint from liquid. The pycnometers were always weighed against a closed counterpoise of nearly the same surface area, made from the same kind of glass. For convenience in weighing, water was introduced into the counterpoise before it was sealed until its weight was slightly less than that of the empty pycnometer (compare Manley, *loc. cit.*). The diameter of the capillary neck at the mark was about 0.3 mm.; the diameter at the point somewhat less.

- If W_p is the true weight of the empty pycnometer in a vacuum,
 W_c " " " " counterpoise in a vacuum,
 V_p " volume of liquid in the pycnometer when filled to the mark,
 V_{pg} " volume of the glass of the pycnometer,
 V_c " external volume of the counterpoise,
 W_1 " apparent weight in air of the empty pycnometer (corr. for air displaced by the brass weights) when weighed against counterpoise,
 W_2 " apparent weight in air of the pycnometer full of water (corr. for air displaced by the brass weights) when weighed against counterpoise,
 W_3 " apparent weight in air of the pycnometer full of liquid (corr. for air displaced by the brass weights) when weighed against counterpoise,
 $\Delta_1, \Delta_2, \Delta_3$ are the densities of air at these successive weighings.
 δ_w is the density of water, and δ_l is the density of liquid at the temperature of the experiment referred to water at 4° .

Then: (1) $W_1 = W_p - \Delta_1 V_{pg} - (W_c - \Delta_1 V_c)$
 (2) $W_2 = W_p + \delta_w V_p - \Delta_2 (V_{pg} + V_p) - (W_c - \Delta_2 V_c)$
 (3) $W_3 = W_p + \delta_l V_p - \Delta_3 (V_{pg} + V_p) - (W_c - \Delta_3 V_c)$.

If: $V_c = V_{pg} + V_p$
 $W_1 = W_p - W_c + \Delta_1 (V_c - V_{pg})$
 $W_2 = W_p + \delta_w V_p - W_c$
 $W_3 = W_p + \delta_l V_p - W_c$
 (4) $\delta_l = \delta_w \frac{W_3 - W_1 + \Delta_1 (V_c - V_{pg})}{W_2 - W_1 + \Delta_1 (V_c - V_{pg})}$.

Thus the calculation of a series of densities becomes very simple if the external volume of the counterpoise is made equal to the sum of the volumes of the glass of the pyknometer and of the liquid it holds when full,* the only fresh quantity involved in each determination being W_3 , the weight of the pyknometer full of liquid corrected for the air displaced by the brass of the weights. [It was pointed out in a recent paper by Gray and Burt (Trans., 1909, 95, 1636) that the difference in density between the platinum and the brass weights is already taken into account in their preliminary standardisation.] The only uncertain factor in equation (4) is Δ_1 , which depends to a small extent on the proportion of water vapour present in the atmosphere. In the case of liquids the density of which is nearly the same as that of water, no appreciable error is introduced by taking Δ_1 as the density of dry air under the conditions of the experiment, but if the density of the liquid falls outside



* In constructing the counterpoise there is no difficulty in making its volume fulfil this condition within 0.5 c.c., and with a little care a closer adjustment is possible. The following figures indicate the error introduced by imperfect adjustment: if the external volume of the counterpoise of a 25 c.c. pyknometer is 0.5 c.c. larger or smaller than that required by the equation $V_c = V_{pg} + V_p$, and the temperature and pressure of the air in the balance case change between the weighings of the pyknometer full of water and of liquid from 10° and 770 mm. to 20° and 740 mm., the error introduced is two units in the sixth decimal place of the density.

the limits 2.0 and 0.85, neglect of the correction may introduce an error into the sixth decimal place of the density.

In the following experiments, pyknometers holding 22 c.c. of liquid were adjusted in a thermostat constant to $\pm 0.01^\circ$, counterpoise and pyknometer being treated in a similar manner before all weighings. The pyknometer and weights were left on the balance with the beam released for fifteen minutes before the final weighing was made (compare Manley, *Phil. Trans.*, 1910, **210**, A, 387), the weight being recorded to 0.01 milligram. The weights were standardised in the way described by Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144).

The accuracy of the method was tested by observing the constancy of W_1 and W_2 on various occasions calculated from equations (1) and (2). The results are given below:

W_1 (grams).	Temp.	Bar. (mm.).	W_2	Temp.	Bar. (mm.).
4.98030	12.0°	776	27.34328	16°	753
4.98027	17.0	740	27.34334	15	745
4.98029	14.0	752	27.34333	15	749
4.98027	16.5	754	27.34333	14	746
			27.34328	14	758

The results of duplicate determinations of the density of four solutions of potassium chlorate at 18° by two pyknometers of form A (see figure), and also of a solution of potassium chloride at 10° by pyknometers of form B, are given in the following table:

Grams KClO_3 in 100 grams of water.	δ_4^{18} by pyknometer I.	δ_4^{18} by pyknometer II.	Mean.
1.8268	1.010044	1.010041	1.010042
0.8428	1.003980	1.003972	1.003976
—	—	1.003977	
0.6102	1.002474	1.002474	1.002474
0.1014	0.999267	0.999269	0.999268
Grams KCl in 100 grams of water.	δ_4^{10} by pyknometer III.	δ_4^{10} by pyknometer IV.	Mean.
0.7273	1.003924	1.003926	1.003925
—	—	1.003924	—

The maximum divergence of any determination from the mean is four parts in a million. In order to obtain this degree of accuracy in the case of liquids with a larger coefficient of expansion than dilute aqueous solutions, more accurate temperature regulation would be required than was used in the above experiments.

The authors wish to express their great indebtedness to Mr. J. J. Manley, Daubeny Curator, Magdalen College, Oxford, for much valuable advice.

CXIV.—*Mannitoboric Acid.*

By JOHN JACOB FOX and ARTHUR JOSIAH HOFFMEISTER GAUGE.

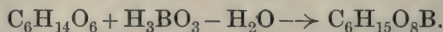
It is well known that the addition of mannitol and other polyhydric alcohols to an aqueous solution of boric acid results in the formation of a comparatively strongly acid liquid; and provided sufficient mannitol is present, boric acid will act as a monobasic acid as regards its titration with sodium hydroxide (Jones, *Amer. J. Sci.*, 1899, [iv], 7, 147). Vignon observed (*Ann. Chim. Phys.*, 1874, [v], 2, 433) that after the addition of borax to solution of mannitol the solution became dextrorotatory, and that the optical activity increased as more borax was added. Similar results were obtained by Bouchardat (*Compt. rend.*, 1875, 80, 120), whilst Müller worked out a method for the estimation of mannitol depending on the alteration in optical activity on the addition of borax to solutions of mannitol (*Bull. Soc. chim.*, 1894, [iii], 11, 329). This peculiarity in the optical activity of mannitol in the presence of borax and also with boric acid suggests the formation of some compound of mannitol and boric acid, for the derivatives of mannitol such as the acetyl are dextrorotatory to a marked extent.

A compound formed by the fusion of mannitol and borax was obtained by Dunstan (*Pharm. J.*, 1883, [iii], 14, 41), and Klein (*Bull. Soc. chim.*, 1878, [ii], 29, 357) described a barium salt which was apparently derived from an acid containing boric anhydride. Both Klein and Bouchardat concluded that a compound of mannitol and borax in equivalent proportions existed in aqueous solutions, but their attempt to obtain the compound yielded only viscous substances.

The tendency of mixtures of mannitol and boric acid to form mannitoboric acid in aqueous solutions is evident from the conductivity measurements of Magnanini (*Zeitsch. physikal. Chem.*, 1890, 6, 58), who drew the conclusion that a compound was formed between one molecule of mannitol and three of boric acid, but so far the mannitoboric acid has not been isolated. From Magnanini's observation as to the decrease of molecular conductivity on dilution and from the measurements of the rotation recorded on p. 1078, it is clear that the compound of mannitol and boric acid is decomposed by water, and it seemed unlikely that a pure substance could be obtained from aqueous solutions. We therefore decided to use alcoholic solutions, and from these we succeeded in obtaining mannitoboric acid in quantity.

Mannitoboric acid separates from the alcoholic solutions in which

it is formed in colourless prisms, melting at 89.5° . Molecular-weight determinations in acetone showed that the acid corresponds with the formula $C_6H_{15}O_8B$, and is derived from one molecule of mannitol and one of boric acid by the loss of one molecule of water:



The fact that only one molecule of each substance takes part in the reaction is in accordance with the behaviour of boric acid mixed with mannitol on titration with alkali, using phenolphthalein as indicator.

All the salts which we have succeeded in preparing, namely, the ammonium, silver, calcium, and barium salts, point to the acid being monobasic. It is, however, possible that other mannitoboric acids containing more than one boric acid residue may exist in alcoholic solutions, but we were unable to detect them in the crystals which separated from such solutions.

The measurements of the optical rotation (p. 1078) are of special interest. It will be seen that the rotation, although small, barely reaches a maximum for alcoholic solutions, but increases continuously, so far as the measurements have been made, with the increase in the concentrations of boric acid when the mannitol is kept constant, as was found by Vignon (*loc. cit.*) for aqueous solutions of mannitol and borax. It is also evident from the results, however, that the effect of any particular proportion of boric acid on the rotation is greater when the concentration of the mannitol is increased. The formation of mannitoboric acid appears, therefore, to be favoured by increasing the concentration of either the mannitol or the boric acid.

EXPERIMENTAL.

Twelve grams of mannitol and 8.2 grams of boric acid were heated with 90 c.c. of absolute or 95 per cent. alcohol under a reflux condenser until all the solid dissolved. The clear liquid was transferred to a stoppered flask in order to prevent evaporation and access of moisture. In a few days a small quantity of mannitol with some mannitoboric acid usually separated, and was removed by filtration. The resulting solution was set aside in a stoppered flask, and after about forty-eight hours considerable quantities of crystals of pure mannitoboric acid were found to have been deposited. These were removed from the liquid, washed with a little alcohol and ether, and dried in the air. The yield from the quantities taken above was 7 grams. The purest products were obtained with 1 molecule of mannitol and 2 of boric acid,

any less quantity of acid resulting in the deposition of a mixture of mannitol and mannitoboric acid, whilst greater proportions of boric acid gave mixtures of mannitoboric and boric acids. Seeding the solution with a crystal of mannitoboric acid hastened the formation of the acid.

When obtained in the manner described, mannitoboric acid consists of tufts of prisms with square ends, melting sharply at 89.5° . Recrystallisation from alcohol could not be effected, since on long boiling the acid was decomposed, mannitol alone being deposited, and the acid is not sufficiently soluble in acetone for practical purposes. Water and phenol were found to decompose the substance. The purity of the acid can, however, be readily checked by the melting point and the determination of the amount of boric anhydride. The latter was estimated by titration with sodium hydroxide, adding more mannitol to the solution, and using phenolphthalein as indicator. In order to prevent volatilisation of boric acid during the combustion, the crystals were mixed with lead chromate:

0.1959 gave 0.2286 CO_2 and 0.1184 H_2O . $\text{C}=31.8$; $\text{H}=6.8$.

0.5200 required 22.65 c.c. $N/10$ -sodium hydroxide. $\text{B}=4.8$.

0.8043 " 36.0 " " $\text{B}=4.9$.

0.2472 " 11.2 " " $\text{B}=5.0$.

$\text{C}_6\text{H}_{15}\text{O}_8\text{B}$ requires $\text{C}=31.8$; $\text{H}=6.7$; $\text{B}=4.9$ per cent.

Determinations of the molecular weight were made, using acetone, as it was found that hydroxylic solvents decomposed the acid:

0.1302 in 22.23 of acetone gave $E=0.032^{\circ}$. $\text{M.W.}=292$.

0.1304 " 22.23 " " $E=0.035^{\circ}$. $\text{M.W.}=292$.

$\text{C}_6\text{H}_{15}\text{O}_8\text{B}$ requires $\text{M.W.}=226$.

Larger quantities of the acid could not be used as the substance is not very soluble in acetone, and no other convenient solvent was available, but the determinations leave no doubt that mannitoboric acid is only slightly associated.

The *ammonium* salt was prepared by covering mannitoboric acid with excess of aqueous ammonia and setting the mixture aside for a few minutes. To the solution alcohol was added so long as a white precipitate continued to form. This settled to a gelatinous mass, but nearly all dissolved on heating on a water-bath. The clear liquid was decanted, and allowed to cool, when a white, crystalline solid separated from the solution. This was collected, and washed with a little alcohol and ether. The crystals changed into a glassy mass on being kept for several weeks:

0.3623 gram was distilled with sodium hydroxide; the liberated ammonia required 15.0 c.c. *N*/10-acid. $\text{NH}_3 = 7.08$.

$\text{C}_6\text{H}_{15}\text{O}_8\text{B}\cdot\text{NH}_3$ requires $\text{NH}_3 = 7.02$ per cent.

Silver, calcium, and barium salts of the acid were prepared by dissolving mannitoboric acid in the calculated quantity of *N*-sodium hydroxide, and adding an excess of an aqueous solution of a soluble salt of the metal. No precipitates resulted until alcohol was added, when in each case a flocculent precipitate was formed. This dissolved on heating the solution, from which the salts separated on cooling as white, crystalline powders. The silver salt darkened rapidly after formation:

Silver salt:—Found, $\text{Ag} = 31.8$. $\text{C}_6\text{H}_{14}\text{O}_8\text{BAg}$ requires $\text{Ag} = 32.4$ per cent.

Calcium salt:—Found, $\text{Ca} = 8.2$. $(\text{C}_6\text{H}_{14}\text{O}_8\text{B})_2\text{Ca}$ requires $\text{Ca} = 8.2$ per cent.

Barium salt:—Found, $\text{Ba} = 21.6$. $(\text{C}_6\text{H}_{14}\text{O}_8\text{B})_2\text{Ba}$ requires $\text{Ba} = 23.4$ per cent.

The salts may also be prepared by grinding the hydroxides with mannitoboric acid and a little water, filtering, and precipitating with alcohol as above. It was not found possible to obtain the barium or lead salt in a perfectly pure condition. The composition of the salts described is not the same as that of Klein's barium salt, $(\text{C}_6\text{H}_{13}\text{O}_9\text{B}_2)_2\text{Ba}$, which appears to be derived from an unknown acid, $\text{C}_6\text{H}_{14}\text{O}_9\text{B}_2$. The salts of mannitoboric acid are much more stable towards water than is the free acid.

Rotation of Solutions of Mannitol and Boric Acid.

Solutions of mannitol in water and absolute alcohol were prepared by heating mannitol and boric acid with the solvent until all the solid was dissolved. The proportion of boric acid to mannitol was increased as long as it could be dissolved, and kept in solution at room temperature. It is noteworthy that mannitol is far more soluble in alcohol when boric acid is present than it is when taken alone.

Aqueous Solutions.

10 grams of mannitol per 100 c.c.

Molecules of boric acid to one molecule of mannitol.	Reading in 2-dcm. tube.
0.8	0°37'
1.5	0 52
2.0	1 2

15 grams of mannitol per 100 c.c.

Molecules of boric acid to one molecule of mannitol.	Reading in 2-dcm. tube.
0.4	0°27'
0.8	1 5
1.0	1 21
1.3	1 38
1.5	1 47

Alcoholic Solutions.

6 grams of mannitol per 100 c.c.

Molecules of boric acid to one molecule of mannitol.	Reading in 2-dem. tube.
1.8	1°40'
2.0	1 52
3.0	2 22
4.0	2 52
5.0	3 3
6.0	3 16

10 grams of mannitol per 100 c.c.

Molecules of boric acid to one molecule of mannitol.	Reading in 2-dem. tube.
2.0	3°28'
2.6	4 14
3.0	4 35
3.5	4 55

12 grams of mannitol per 100 c.c.

Molecules of boric acid to one molecule of mannitol.	Reading in 2-dem. tube.
2.2	4°51'
3.0	6 2
4.0	6 56

The readings were taken at room temperatures (17° to 19°), moderate variations in temperature having little effect on the rotation. A part of the alteration in the rotation may arise from changing the solvent, but there can be no doubt that the lower results in water are mainly due to the effect of the water in splitting up or preventing the formation of mannitoboric acid.

EAST LONDON COLLEGE.

CXV.—*The Course of Chemical Change in Quinol Under the Influence of Radiant Energy.*

By WALTER NOEL HARTLEY and OTWAY HENRY LITTLE.

THE experimental work on which one of us has been engaged for some years past appears to support, if not to afford, proof of the hypothesis that the intra-molecular vibrations of many organic substances are actuated by the radiant energy to which they are subjected during the examination of their spectra, or, in less exact terms, by exposure to light. The facts which give support to this view are, that light actually causes chemical combinations and decompositions, and also such changes in properties as amount to modifications in constitution. It is believed that such changes are not of rare or exceptional occurrence, but are frequently in evidence by the production of tautomeric and isomeric substances.

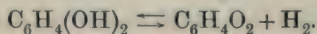
A prominent instance was the effect of light on aqueous solutions

of *p*-benzoquinone, the changes occurring chiefly in the visible spectrum and during the short period when the solutions were actually under observation, to an extent which modified the composition of the substance under examination. Similarly, it was proved that alcoholic solutions of *p*-benzoquinone underwent reduction to quinol (Hartley and Leonard, *Trans.*, 1909, **95**, 34).

Evidence of the chemical reactions induced by the solvents alcohol and water was afforded by their molecular-vibration curves; and from similar evidence it was concluded that quinhydrone does not undergo dissociation when dissolved in alcohol, for although it shows absorption bands corresponding with those of both its constituent substances, quinol and *p*-benzoquinone, the bands are modified. To account for the great difference in the spectrum of *p*-benzoquinone and that of benzenoid derivatives, it is necessary to contrast the effect of the replacement of hydrogen in benzene by other hydrocarbons (namely, the coalescence of the narrow bands and their more diffuse character) with the effect of the ketonic complex in substances other than benzene, such as oximino-ketones, diureides, and camphor.

The ketonic band is always broad and somewhat diffuse, and it appears only in concentrated solutions; it also disappears easily on dilution (*Trans.*, 1905, **87**, 1791). With two ketonic groups in the molecule the absorption band is intensified. By the combined effect of two such characteristic absorption phenomena as the ketonic and the benzenoid in one molecule, we obtain the curve for *p*-benzoquinone (*Brit. Assoc. Reports*, 1901-02).

To restrict the conditions of experiment to the action of radiant energy solely, it became necessary to eliminate the chemical action of the solvents water and alcohol; to this end, observations were made on solutions in ether, and on the vapours of pure substances. The result of this investigation was the discovery of a reversible chemical reaction in the sense of the equation:



A further examination of the conditions of this reaction was commenced, as it appeared to be possible, by photographing the absorption spectra of quinol at different stages of the change, to ascertain the quantity of *p*-benzoquinone formed under different conditions of temperature and of exposure to light, by means of the differences in the absorption. Preliminary experiments on definite mixtures of *p*-benzoquinone and quinol proved that owing to the nature of the absorption exerted by the latter substance, small quantities of *p*-benzoquinone could not be estimated in this manner. A method of volumetric analysis dependent on the liberation of iodine from hydriodic acid was also tried, but this

did not prove quite satisfactory, owing to the impossibility of distinguishing between *p*-benzoquinone and quinhydrone, as both have the same oxidising action. Observations were then made in closed flasks by measuring the increase of pressure and of volume of the contents of the flasks, and finally determining the volume of the hydrogen evolved in the reaction by exploding the gas with the air in the flask and measuring the contraction. Assuming that the rays of high refrangibility are the most active, rather than the coloured rays or those in the infra-red, the first experiments were made in darkness, and subsequently under different intensities of illumination, in vessels of glass and of quartz.

EXPERIMENTAL.

Preparation of Pure Quinol.

Eighty grams of well-crystallised quinol were purified by the treatment already described (Hartley and Leonard, *Trans.*, 1909, **95**, 49), but the solutions were evaporated and recrystallised in a vacuum. The product was recrystallised from hot water and dried. The quinol melted sharply at 170.3° .

1st Series: Experiments in Darkness.

One milligram-molecule (0.110 gram) of quinol was weighed into each of six 300 c.c. glass flasks. Two flasks were filled with dry air, two with dry hydrogen, and two with dry oxygen. They were all heated in the dark room for twenty minutes to $145\text{--}150^{\circ}$, being embedded in a bath of kieselguhr, and the temperature measured by thermometers placed in the flasks with their bulbs from 2 to 3 cm. above the bottom. The quinol condensed on the neck of the flask in long, colourless crystals, but no change could be detected in the contents of any of the flasks.

One flask containing oxygen, which had remained in the dark room overnight, was re-heated for twenty minutes to $150\text{--}160^{\circ}$. On cooling, the film of crystals which formed on the inside of the flask appeared slightly fluorescent in daylight.

After remaining for a week in the dark room, one of the flasks filled with air was re-heated for two and a-half hours to 170° . When it had cooled, most of the quinol had condensed on the neck of the flask in long, white crystals, but along the thermometer for a distance of about 1 cm. from the cork some bronze-green crystals of quinhydrone had formed.

2nd Series: Vapour Exposed to Spark Rays.

One milligram-molecule of quinol was heated in a globular quartz distilling flask, 10 cm. in diameter, filled with oxygen, which was placed in a bath of kieselguhr and maintained at a temperature of 150° for twenty-five minutes, during which time it was exposed to the spark rays of cadmium.

On examination when cooled, the upper portion of the bulb was seen to be covered with a purple, crystalline film, which showed green in parts, especially by transmitted light. This film was fluorescent, and appeared violet-gray by ordinary daylight, the violet being due to fluorescence. On the bottom of the flask a reddish-brown substance was seen in thin layers. In the side-tube (which entered the distilling flask about 55 mm. from the bulb) some thin, crystalline plates, 0.5 to 1 mm. across, having a bronze, metallic lustre were deposited. The colour and form of the crystals showed that the substance was undoubtedly quinhydrone, freed from quinol by sublimation. In the flask the quinol was seen in colourless, glistening crystals.

The gray substance was distinct from the quinol; it was crystalline, and was deposited in a separate layer on the upper interior surface of the globe and up the neck of the flask for about 2 cm. When seen by yellow light, or by the incandescent gas light (Welsbach), its colour was gray, but in a powerful light the gray material showed a beautiful display of iridescent colours exactly like that of the feathers of a peacock. The violet colour was seen only in the daylight or by the light of the spark, which is suggestive of its being due to fluorescence. The crystals contained in the side-tube were volatilised by heat, and condensed on a cold watch glass. The condensed vapour had exactly the same colour and characteristic appearance as the crystalline film on the upper interior surface of the flask.

The experiment was repeated, using the same quartz flask, which was heated to 150° and exposed to the spark rays for twenty-five minutes. All the quinol showed the violet-gray fluorescence, and on remaining for half an hour at the temperature of the air, some of the crystals became bronze-green, and were evidently quinhydrone.

The experiment was again repeated.

The flask was placed in an air-bath packed with asbestos cloth, and heated until the temperature reached 147° . The stream of sparks was then switched on, and the temperature kept within the limits 147 — 155° . After five minutes a brownish-violet deposit was seen (by the light from the spark) to be forming on the top of

the bulb close to where the sparks were passing. The sparks passed continuously for thirty minutes. When cool, the flask was removed, and golden-yellow crystals of *p*-benzoquinone were found on the cork and on the thermometer and neck of the flask for about 2 cm. from the cork. The odour of *p*-benzoquinone was very distinct. The neck of the flask was covered with a deposit of bronze-green and violet fluorescent crystals. On the inside of that portion of the flask which was nearest to the spark, a thin, reddish-brown film remained after the flask was washed out with ether. This film did not dissolve in cold or hot water, in cold or hot dilute acids, but was readily soluble in very dilute cold sodium hydroxide. It was evidently the substance examined by Hartley and Leonard (*loc. cit.*).

3rd Series: Experiments in Diffused Daylight.

Experiments were made in order to observe the formation of the different films on cooling. Flasks containing 1 milligram-molecule of quinol were heated to 170° in the same manner as in the last experiment, but the time of heating was varied from one and a-half to three hours. When the heating was finished, the asbestos cloth was removed, and the formation of the crystals observed. On the neck and upper portion of the flask a film appeared, which was quite white at first, but as it cooled it showed a violet-gray fluorescence, then an increasingly deeper violet, until, finally, portions of it became bronze-green on remaining for some time at the temperature of the air. This was evidently due to the condensation of the quinol first, after which the *p*-benzoquinone condensed and combined to form quinhydrone. With prolonged heating a greater quantity of *p*-benzoquinone was produced, and the above changes followed one another more rapidly while cooling was in progress, the *p*-benzoquinone finally condensing on the very top of the neck or in the side-tube. When the lower portion of the bulb of a flask which had been heated for three hours was cooled quickly by placing it in a vessel of cold water, a thin, yellow film of *p*-benzoquinone crystals was formed on the bottom of the bulb. The violet fluorescent crystals were deposited on the lower part of the neck, and quinhydrone all over the top of the neck. The *p*-benzoquinone formed in all these experiments disappeared on allowing the flask to remain for from three to ten days, the time depending on the amount of *p*-benzoquinone present. It was probably changed into quinhydrone by combination with the vapour of the quinol.

The reddish-brown film always occurred near the source of radiant energy or on the very bottom of the flask, where the temperature

was greatest. It appears in the latter case to be formed by the quinol melting on a portion of the flask, heated above the melting point of quinol, but subsequent experiments showed that this film volatilised on prolonged heating, and was deposited as quinhydrone. The spark was always situated outside at the top of the bulb and 2 or 3 cm. away from it. The temperature inside the flask at this point, due to the source of heat, was below the melting point of quinol, but the radiant energy (of short wave-length) from the spark produced the same effect as the higher temperature at the bottom of the flask.

4th Series: Experiments in Diffused Daylight.

Experiments were performed in order to observe the changes taking place as the quinol was subjected to a rising temperature. An air-bath was formed of a litre beaker from which the bottom had been knocked out; this in some experiments was placed on a piece of wire gauze covered with asbestos, and in others on a sand-bath. A half-litre glass distilling flask containing 1 milligram-molecule of quinol was placed inside the beaker, the bottom of the flask being 2 or 3 cm. from the asbestos or sand. The whole was exposed to diffused daylight, and the changes taking place during heating were noted. The quinol at first sublimed and condensed on the upper portion of the bulb and bottom of the neck, but when the rising temperature indicated by the thermometer was 120° , the first trace of the violet fluorescence appeared on a few crystals. When the temperature reached 140° this had considerably increased, and at 165° some quinhydrone had condensed on the neck, which was well above the beaker, and therefore cooler than the bulb. The amount of condensed quinhydrone increased until, when the temperature was 180° , some *p*-benzoquinone appeared on the top of the neck and in the side-tube. On cooling, after prolonged heating, the *p*-benzoquinone condensed on the top of the neck and at some distance along the side-tube, the quinhydrone on the lower part of the neck with a fringe of violet fluorescent crystals below.

5th Series: Experiments in Darkness.

One milligram-molecule of quinol was heated in a litre glass flask. The air-bath used was formed of an inverted, hollow, truncated cone of sheet-iron, in the bottom of which some sand was placed. The flask was suspended so as not to touch the sand in the bottom of the bath, and strips of asbestos were placed between it and the inside of the bath. The neck and upper portion of the flask were covered with asbestos cloth to keep the temperature uniform, and

also to prevent any light from the burner reaching the contents. The temperature was measured by a thermometer inserted into the flask, the bulb being 2 to 3 cm. from the bottom of the flask.

This method of heating was adopted in all subsequent experiments, and in every experiment care was taken to have the flask and contents thoroughly dry. When cold, the flask was examined in daylight.

Experiment (1):—One milligram-molecule of quinol was heated for three hours, the temperature being kept within the limits 160—170°.

Along the neck of the flask some isolated prisms of quinol and irregular plates and clusters of quinhydrone were seen, whilst towards the bottom of the neck there were some plates of quinhydrone and a mixture of long fine prisms, also a few plates of quinol.

Under the microscope, some of the prisms of quinol, although showing violet fluorescence on parts of their surface, were in these portions transparent, the rest of the crystal being covered by a film composed of tufts of quinhydrone crystals standing out perpendicularly from the quinol prisms.

A separate portion of about 6 sq. cm. of the top of the bulb was covered with a violet fluorescent film, surrounded by scattered, irregularly-shaped crystals of quinhydrone. The microscope showed the violet film to be composed of short prisms in the centre, the edge being formed of long needles, which were dark violet in colour.

Experiment (2):—One milligram-molecule of quinol was heated for three hours, the temperature being kept within the limits 150—160°.

At the top of the neck of the flask there were a few crystals of quinhydrone, with some crystals of quinol. Lower down, on some of the long prisms of quinol, tufts of fine quinhydrone crystals had formed. At the bottom of the neck there was a thin film composed of a mixture of fine crystals of quinhydrone and prisms of quinol, and on the upper surface of the bulb three separate small patches of the violet fluorescent film had formed. The violet crystals appeared as short prisms under the microscope.

The total change was less than in the preceding experiment, there being a greater amount of unchanged quinol.

Experiment (3):—One milligram-molecule of quinol was heated for three hours, the temperature being kept within the limits 130—140°.

No crystals condensed above the side-tube, but below this some small needles of quinol had formed, many of which were dark violet (almost black) on the surface. At the bottom of the neck

the film was very fine, and consisted of quinol and a little quinhydrone. The quinhydrone appeared to have formed the larger crystals, but under the microscope these were seen to consist of clusters of very fine crystals, whilst the quinol was in separate prisms. On the upper surface of the bulb there was a very thin film of quinol with violet crystals scattered through it, some of which were greenish-gray (almost black) by reflected light.

The total amount of quinol unchanged was much greater than in the last experiment.

Experiment (4):—One milligram-molecule of quinol was heated for eleven and a-half hours, the temperature being kept within the limits 150 — 160° until the last hour of heating, when it rose from 159° to 172° .

Long, bronze-green needles, with violet fluorescent plates, and prisms of quinol were formed at the top of the neck, and at the bottom a few plates of quinhydrone mixed with plates and prisms of quinol, many being violet on the surface. On the bulb there was a very thin film of quinol, showing a little violet in parts. About one-half the quinol remained unchanged.

From this it would appear that very little change took place until the last hour of heating, the quinol merely subliming and condensing under the different conditions prevailing at different positions on the neck of the flask. As some of the crystals of quinol were violet on part only of their surface, the remainder being unchanged, it is probable that the long, bronze-green needles were not completely converted into quinhydrone, but contained a central portion of unchanged quinol, the heating at the higher temperature not being continued long enough to cause the quinol needles to break down and form the usual clustered plates of quinhydrone.

6th Series: Vapour Exposed to Spark Rays.

One milligram-molecule of quinol was heated in a half-litre quartz flask, and after the temperature had risen to the required degree, the spark rays of cadmium were switched on. The flask was connected to a manometer, the barometric pressure and the pressure and temperature in the flask being read, both before and after heating. The liberated hydrogen was exploded with the air in the flask, and from these readings the increase in volume was calculated. The figure given is the mean of three results in each case.

In all cases *p*-benzoquinone, quinhydrone, and violet fluorescent crystals were formed, and at temperatures above 160° all the quinol was changed, at least on the surface.

The amount of quinhydrone which would be formed if the change

that took place were simply the conversion of quinol into quinhydrone was also calculated.

Temperature.	Time exposed to spark rays.	Greatest pressure in flask, in mm. of mercury.	Increase in volume, reduced to N.T.P.	Calculated amount of quinhydrone.
1 150—155°	25 mins.	954·6	2·5 c.c.	0·112 mg.-mol.
2 150—155	30 „	1091·4	2·6 „	0·117 „
3 150—160	15 „	1070·9	2·5 „	0·112 „
4 150—160	30 „	781·3	4·5 „	0·201 „
5 150—160	45 „	1074·0	5·3 „	0·237 „
6 160—170	20 „	1075·9	2·4 „	0·108 „
7 160—170	40 „	891·0	4·4 „	0·197 „

7th Series: Experiments in Diffused Daylight.

One milligram-molecule of quinol was heated in glass flasks in diffused daylight. The crystals formed were dissolved out of the flask with ether, the ether evaporated off by blowing a current of cool air over it, and 25 c.c. of freshly prepared hydriodic acid solution added. The whole was diluted to about 1½ litres, and the amount of iodine liberated was found by titrating with sodium thiosulphate. The volume of hydrogen given off was then calculated, and also the amount of quinhydrone which would be formed if the conversion of quinol into quinhydrone were the only change that occurred.

Greatest temperature.	Time of heating.	Crystals in flask after heating.	Calculated vol. (at N.T.P.) of hydrogen liberated.	Calculated amount of quinhydrone.
1. 170°	3 hours	{ All quinhydrone except a few violet crystals }	4·63 c.c.	0·207 mg.-mol.
2. 193	3 „	{ Do. do. }	6·50 „	0·291 „
3. 205	2 „	{ About equal amounts of quinone and quinhydrone }	6·72 „	0·301 „
4. 180	16 „	{ Do. Do. }	5·73 „	0·256 „
5. 190	15 „	{ Quinhydrone and violet crystals }	5·84 „	0·261 „

Heated in a Bath of Glycerol.

6. 135° for	4 hours			
then rising slowly to 170°	6 „	{ Some quinhydrone and quinol. }	2·29 c.c.	0·103 mg.-mol.

Heated in a Bath of Sulphuric Acid.

7. 100—160°* 30 hours in 10 stages of three hours each. $\left\{ \begin{array}{l} \text{Quinol, a little quin-} \\ \text{hydrone and violet} \\ \text{crystals. No change} \\ \text{below } 145^{\circ} \end{array} \right\}$ 1.22 c.c. 0.059 mg.-mol.
8. 160—170° 32 hours $\left\{ \begin{array}{l} \text{Quinol, a little} \\ \text{quinhydrone and} \\ \text{quinone} \end{array} \right\}$ 3.50 ,, 0.157 ,,

* 18 hours below 145°.

8th Series: Under Diminished Pressure.

One milligram-molecule of quinol was heated in a litre glass distilling flask in diffused daylight, but the flask was almost completely protected from the action of light by a covering of asbestos cloth. The flask was exhausted, and the pressure read by means of a mercury manometer, which was not detached during heating.

Experiment 1.

Heated for three hours, the temperature being kept within the limits 170—185°.

Before heating.		After heating.	
Pressure	= 18.6 mm.	Pressure	= 22.7 mm.
Temperature	= 13.8°.	Temperature	= 14.2°
Volume of gas in flask	} = 23.15 c.c. at N.T.P.	Volume of gas in flask	} = 28.68 c.c. at N.T.P.

Increase in volume = 5.53 c.c. at N.T.P.

The flask was uncovered when the heating was completed, and when the temperature had remained stationary at 14.2° for some time the readings were taken. The crystals in the flask were all violet fluorescent prisms, but on remaining until next day, exposed to diffused daylight and under diminished pressure, they were found to be practically all converted into quinhydrone. Pressure and temperature readings were again taken, but no change had occurred in the volume.

Experiment 2.

Heated for four hours, the temperature being kept within the limits 147—153°.

Before heating.		After heating.	
Pressure	= 23.7 mm.	Pressure	= 27.3 mm.
Temperature	= 15.1°.	Temperature	= 15.2°.
Volume of gas in flask	} = 29.84 c.c. at N.T.P.	Volume of gas in flask.	} = 34.36 c.c. at N.T.P.

Increase in volume = 4.52 c.c. at N.T.P.

All the quinol condensed as violet fluorescent crystals, but none of it was converted into bronze-green quinhydrone crystals, even on remaining for twenty-four hours exposed to diffused daylight.

Experiment 3.

Heated for two hours and twenty minutes to 163°, and on the following day for seven hours and ten minutes to 165°.

	Pressure.	Temperature.	Volume of gas in flask.
Before first heating	20·3 mm.	14·0°	25·66 c.c. at N.T.P.
After „ „	22·4 „	14·0	28·31 „ „
Before second „	22·5 „	13·5	28·51 „ „
After „ „	25·6 „	13·5	32·41 „ „

Therefore heating for 2 hours 20 min. to 163° gave an expansion of 2·65 c.c. at N.T.P., and heating for an additional 7 hours 10 min. to 165° gave an expansion of 3·90 c.c. at N.T.P.

Total expansion for 9 hours 30 mins. = 6·55 c.c. at N.T.P.

The flask was protected from the action of light until cool; only violet fluorescent crystals were formed; even after remaining for five days exposed to diffused daylight these had not changed to bronze-green quinhydrone crystals.

9th Series: Under Diminished Pressure, in Darkness.

One milligram-molecule of quinol was heated in an air-bath packed with asbestos cloth. The pressure in the flask was reduced by means of an air pump, and measured by a mercury manometer. The flask was sealed by stout pressure tubing and a strong screw-clip. It was detached from the manometer, and taken to the dark room for heating. It was allowed to cool in the dark, and then attached to the manometer, the mercury tube being exhausted and sealed before the clip on the tube connecting it with the flask was opened.

Experiment 1.

Heated for three hours, the temperature being kept within the limits 147—158°, and at 14° the pressure was 20 mm.

The quinol was totally unchanged, the crystals did not even show violet fluorescence, and the pressure readings showed no appreciable change in volume.

Experiment 2.

Heated for five hours, the limits of temperature being 159—168°, and at 17·7° the pressure was 18 mm.

There was no change in the appearance of the quinol; neither

crystals of quinhydrone nor violet fluorescent crystals could be detected. The volume had increased only about 0.5 c.c.

Experiment 3.

The flask after the conclusion of the last experiment was kept exhausted, and allowed to remain in the dark for four days. No change having occurred in that time, it was re-heated for five and a-half hours, the temperature being kept within the limits 170—189°, and at 17° the pressure was 16 mm.

On the upper portion of the neck of the flask there were long prisms of quinol, with a few scattered clusters of quinhydrone crystals. On the lower portion of the neck the prisms of quinol were more thickly grouped, while at the bottom they were mixed with some plates of quinol. There were no violet crystals, and the increase in volume was not more than 1 c.c.

Summary of Results.

In total darkness, prolonged heating at temperatures varying between 150° and 160°, and also between 160° and 170°, and for periods varying between two and a-half and three hours, produced very little, if any, change in quinol.

In diffused daylight, in vessels both of quartz and of glass, prolonged heating at 150° produced very little change; at temperatures between 165° and 170° a large proportion of quinhydrone was formed.

By the light of the electric spark (from cadmium electrodes), such as is used in photographing absorption spectra, the action was more vigorous, and especially when quinol was contained in quartz vessels; *p*-benzoquinone and quinhydrone are both produced and condensed in distinct and separated groups of fine crystals. The quinhydrone was always in larger proportion than the *p*-benzoquinone, which indicated that the former is an intermediate product in the formation of *p*-benzoquinone.

None but a very feeble action occurs below 160°; this was first noticed by the quinol appearing in two forms in the flasks. Firstly, in the usual long, white crystals, and secondly, in films of small crystals of microscopic dimensions, which are mixed with minute quantities of crystals of quinhydrone. It is these small quinol crystals which appear to change to quinhydrone. The change has been observed to take place in two stages. The small crystals show a violet fluorescence on the surface, which becomes a dark purple colour, almost black, then bronze-green, while still retaining the

form of quinol crystals. The violet fluorescent substance was formed in small quantities under conditions which yielded scarcely a trace of any other product.

Conclusions.

(1) The reaction seems to attain a condition of equilibrium when 0.6 of a milligram-molecule of quinol has lost 6.7 c.c. of hydrogen, and the principal product is quinhydrone.

(2) The reaction is not strictly reversible in presence of air or oxygen, because under no conditions does the quinhydrone revert to quinol unless an atmosphere of hydrogen be provided.

(3) In a flask containing crystallised quinol, quinhydrone, and *p*-benzoquinone, exposed to daylight, the *p*-benzoquinone soon disappears, its vapour reacting with the residual quinol to form quinhydrone.

(4) In every instance the most complete and rapid chemical change was effected by rays of shortest wave-length.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

CXVI.—*The Intramolecular Condensation of Aromatic Sulphinic Acids. Part II. The Interaction of Aromatic Disulphoxides and Sulphuric Acid.*

By THOMAS PERCY HILDITCH.

THE action of cold concentrated sulphuric acid on aromatic sulphinic acids or their chlorides has been shown (Trans., 1910, **97**, 2579) to be largely dependent on the nature of the substituents in the benzenoid residues of the latter compounds; when few substituents (none of which occupy a position para- to the thionyl group) are present, considerable quantities of dioxides of diphenylene *p*-disulphide may be formed, whilst with more complex molecules the only products definitely isolated are small amounts of disulphoxides. In the same communication it was pointed out that the various previous syntheses of diphenylene *o*-disulphide were probably (from analogy to the condensation of a sulphinic acid to a dioxide of diphenylene *p*-disulphide) due to the condensation of temporarily produced sulphonylic acid derivatives of the type $R \cdot S \cdot OH$.

Since, as is well known, the simplest products of autoxidation and condensation of the sulphinic acids are the disulphoxides, formulated alternatively as $R \cdot SO \cdot SO \cdot R$ or $R \cdot SO_2 \cdot S \cdot R$, the decomposition of these substances has been studied with the aim of throwing further light on the nature of the sulphinic and sulphonylic

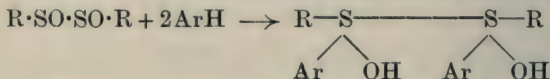
condensations. Three types of disulphoxide have been employed, and different results have been obtained in each case, indicating that here again the influence of substitution is very strongly marked:

(a) *Non-substituted*.—Diphenyl disulphoxide.

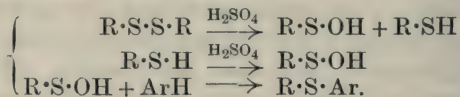
(b) *Para-substituted*.—Di-*p*-phenetyl disulphoxide.

(c) *Multi-substituted*.—Di-*p*-tolyl methyl ether disulphoxide.

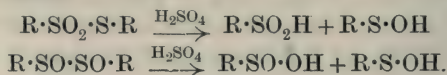
The behaviour of each compound has been studied in cold concentrated sulphuric acid solution (i) alone, and (ii) in presence of a phenolic ether. The latter case will be first considered, for in this instance condensation frequently takes place with formation of sulphonium bases, in much the same way as that found by Smiles and Le Rossignol (*Trans.*, 1906, **89**, 696) in the case of simple aromatic monosulphoxides. There are, however, several possibilities besides that of direct condensation at each thionyl group of the true disulphoxide $R \cdot SO \cdot SO \cdot R$ (which is, as a matter of fact, shown by the analytical data not to occur):



It has been found recently by Prescott and Smiles (this vol., p. 640) that aromatic disulphides, $R \cdot S \cdot S \cdot R$, undergo condensation with phenolic ethers, etc., in concentrated sulphuric acid solution through hydrolytic fission of the disulphide molecule; and although no direct evidence of the existence of the above-mentioned sulphoxylic compounds, $R \cdot S \cdot OH$, is yet available, these authors have shown that it is certain that in this instance the condensation which occurs takes place between a sulphonylic derivative and the phenolic ether:



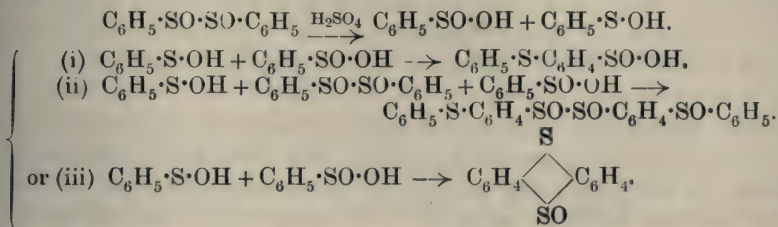
Evidently a similar hydrolytic decomposition may occur in the case of aromatic disulphoxides, such decomposition leading (according to either of the disputed formulæ) to a mixture of sulphonylic and sulphinic acids:



Condensation might then ensue with both parts of the hydrolysed disulphoxide, leading to a mixture of an aromatic sulphonium salt and an aromatic sulphide:



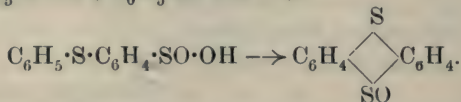
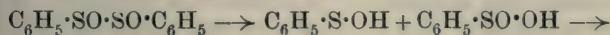
On the other hand, further intermolecular condensation could take place before reaction with the phenolic ether; and here there are three possibilities, as may be readily seen from the example of diphenyl disulphoxide:



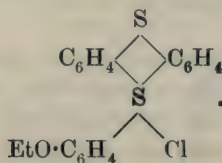
Each of these alternative decompositions has been met with in one or other of the disulphoxides studied, indicating that, although the subsequent decomposition is largely conditioned by the nature and position of the other substituents in the benzenoid residue, the first step in the reaction in concentrated sulphuric acid solution is that of the above fission of the disulphoxide molecule.

This will be best realised by consideration of the individual cases investigated.

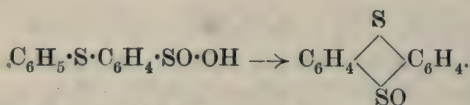
(a) The non-substituted diphenyl disulphoxide, when dissolved in concentrated sulphuric acid alone for some time, gave a mixture of two products of known constitution, namely, a considerable quantity of the monoxide of diphenylene *p*-disulphide, together with a much smaller amount of the ortho-isomeride. The course of the reaction was accordingly:



When condensed in presence of phenetole, however, a mixture of sulphonium bases was produced, from which two platinichlorides were isolated in a pure condition. The salt obtained in greater quantity melted at 130°, and corresponds with a sulphonium chloride of the formula $(\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}_6\text{H}_4)(\text{C}_2\text{H}_5\text{O}\cdot\text{C}_6\text{H}_4)_2\text{SCl}$, whilst a small amount of a salt of higher melting point (191°) was also formed, corresponding with a chloride:



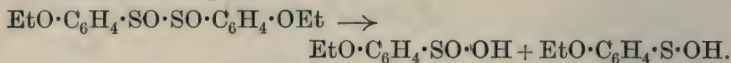
It appeared, then, that the rate of condensation of phenetole with the intermediate product $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{SO}\cdot\text{OH}$ was appreciably greater than that of the final condensation in the diphenylene disulphide synthesis:



The diphenylene disulphide monoxides formed in the first experiment were also condensed separately with phenetole in sulphuric acid. It was found that neither the *o*- nor the *p*-isomeride yielded any sulphonium base, although both underwent some alteration, possibly owing to sulphonation or similar subsidiary reaction. In either case, however, a considerable proportion of the unchanged monoxide was recovered, as was anticipated from the fact that the colours of the solutions in sulphuric acid were not altered on addition of phenetole.

It therefore seems natural to suppose that the formation of the cyclic sulphonium derivative is due to condensation of the primary product of reaction with phenetole.

(b) The para-substituted di-*p*-phenetyl disulphoxide does not suffer intermolecular condensation when dissolved alone in sulphuric acid, and was recovered therefrom unchanged. When phenetole is also present, however, abundant evolution of sulphur dioxide occurs, and triphenetylsulphonium is, except for a very small quantity of diphenetyl sulphide, the only product. Hence it must be supposed that in this instance the sulphonylic derivative is oxidised to sulphinic or sulphonic acid by the sulphuric acid, and no preliminary condensation takes place:



It was hoped that the remaining phase of the simplest form of the condensation reaction (formation of aromatic sulphides from the sulphonylic portion of the decomposed disulphoxide) might have been accomplished by the condensation of di-*o*-carboxyphenyl disulphoxide to thioxanthone by means of benzene in sulphuric acid, since *o*-carboxybenzenesulphinic acid furnishes that substance under similar conditions (Davis and Smiles, *Trans.*, 1910, **97**, 1292). It was found impossible, however, to prepare this compound by the usual means.

(c) An example of a multi-substituted disulphoxide was found in di-*p*-tolyl methyl ether disulphoxide. This substance, when dissolved alone in concentrated sulphuric acid, was found to condense, not to a derivative of diphenylene disulphide, but to a compound

formed in accordance with method (ii) (p. 1093). The same substance was also formed in sulphuric acid solution in presence of *p*-tolyl methyl ether, whence it appears that the numerous substituents inhibit in this case the formation of a sulphonium base (compare Smiles and Le Rossignol, *Trans.*, 1908, **93**, 751). The reduced reactivity of the disulphoxide system in this compound is further indicated by its failure to undergo reduction by hydriodic acid in acetic acid solution at 100°, a reagent which transforms disulphoxides in general into the corresponding disulphides (Hinsberg, *Ber.*, 1908, **41**, 4294).

This investigation proves, therefore, that the interaction of aromatic disulphoxides with sulphuric acid proceeds on the same general lines as that of aromatic disulphides with the same reagent, and also illustrates once more the great influence of substitution on the capacity for condensation of aromatic sulphides and sulphoxides. Taken in conjunction with the work of Prescott and Smiles (*loc. cit.*), it affords further evidence, moreover, in favour of the view that the formation, not only of the open-chain condensation products of disulphides and disulphoxides, but also of the heterocyclic diphenylene disulphide derivatives, is due to the intermediate production and subsequent condensation of sulphonylic and sulphinic acids.

EXPERIMENTAL.

Condensation of Diphenyl Disulphoxide in Concentrated Sulphuric Acid.

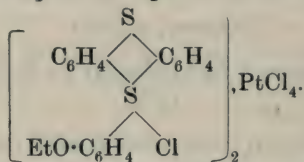
Five grams of diphenyl disulphoxide were dissolved with shaking in cold concentrated sulphuric acid, and set aside for some time. The solution, at first almost colourless, gradually changed through pale green to a deep bluish-green, and finally to an almost black liquid. When no further change could be detected, the whole was mixed with ice-water, and a cream-coloured solid separated. This was collected, dried, and extracted several times with boiling alcohol. The alcoholic extracts deposited white crystals on cooling, and after recrystallisation the latter melted at 146–148°. A mixture of this substance with diphenylene *o*-disulphide monoxide (Part I., *loc. cit.*) melted at 145–148°, and the identity of the substance was further confirmed by analysis. (Found, C=62.09; H=4.22. Calc., C=62.07; H=3.45 per cent.)

A considerable portion of the product was, however, insoluble in hot alcohol. This was boiled with acetic acid, and dried at 130° for analysis; it melted indefinitely at 180–185°, and was found to be the monoxide of diphenylene *p*-disulphide. (Found, C=62.88; H=3.38.)

Condensation of Diphenyl Disulphoxide with Phenetole in Concentrated Sulphuric Acid.

Five grams of the disulphoxide were dissolved in sulphuric acid as before, and a few drops of phenetole added; an intense greenish-blue coloration was produced, which ultimately became faint reddish-brown after excess of the phenolic ether had been added. Very little sulphur dioxide was evolved during the reaction, indicating the absence of any oxidation.

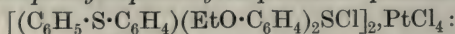
The reaction mixture was poured into ice-water, and extracted with ether to remove phenetole and any non-basic products (in this case a very small amount of a semi-solid substance, which was not further investigated). The aqueous extract, consisting of a turbid solution of sulphonium sulphates, was then heated to boiling, neutralised with barium carbonate, and filtered. The clear filtrates were acidified with hydrochloric acid, and mixed with an aqueous solution of chloroplatinic acid. A copious buff precipitate appeared, and this was collected, dried, and dissolved in as small a quantity as possible of epichlorohydrin. On the addition of alcohol, a brown powder was precipitated. This was collected, and after further purification, melted at 191° ; analysis showed it to be *thio-diphenylenephenetylsulphonium platinichloride*:



0.0782 gave 0.1290 CO_2 and 0.0189 H_2O . $\text{C}=44.99$; $\text{H}=2.69$.

$\text{C}_{40}\text{H}_{34}\text{O}_2\text{S}_4\text{Cl}_6\text{Pt}$ requires $\text{C}=44.36$; $\text{H}=3.15$ per cent.

The alcohol-epichlorohydrin filtrates deposited on spontaneous evaporation a second pale brown, crystalline salt, which, after drying at 100° , melted at 130° . Phenyldiphenetylsulphonium platinichloride melts at $135\text{--}137^{\circ}$ (Smiles and Le Rossignol, *loc. cit.*), but equal proportions of this compound and the salt now obtained melted indefinitely at $100\text{--}115^{\circ}$. The distinct nature of the latter salt was also proved by analysis, which showed that it was *phenylthiolphenyldiphenetylsulphonium platinichloride*:



0.1708 gave 0.3160 CO_2 and 0.0544 H_2O . $\text{C}=50.47$; $\text{H}=3.54$.

0.1708 ,, 0.0248 Pt. $\text{Pt}=14.52$.

$\text{C}_{56}\text{H}_{54}\text{O}_4\text{S}_4\text{Cl}_6\text{Pt}$ requires $\text{C}=50.68$; $\text{H}=4.07$; $\text{Pt}=14.71$ per cent.

Condensation of Diphenylene o- and p-Disulphide Monoxides respectively with Phenetole.

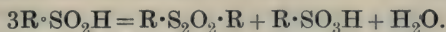
The monoxide of diphenylene *o*-disulphide dissolves freely in concentrated sulphuric acid, forming a deep purple-red solution. Addition of phenetole produced no alteration in the colour of the solution, even when added in excess, and allowed to remain for half an hour. On pouring the mixture into cold water, a sticky solid separated, which was completely soluble in ether. After removal of the ether and phenetole, an oily residue was left, which on recrystallisation from alcohol gave the original diphenylene *o*-disulphide monoxide, melting at 148° , together with small amounts of a substance of less definite nature. No sulphonium base could, however, be detected.

A similar conclusion was reached with diphenylene *p*-disulphide monoxide; this compound is less readily soluble in sulphuric acid, to which it imparts a dull greenish-brown hue, and the greater portion was recovered unchanged after addition of phenetole, no sulphonium base being formed.

Di-p-phenetyl Disulphoxide.

This compound was prepared by the method which was found most suitable for the preparation of dicamphoryl β -disulphoxide (Trans., 1910, **97**, 1091), and which has since been proved to be of general application. It is based on the superior catalysing action of hydriodic acid, by comparison with other mineral salts, on a sulphinic acid.

Thus, 10 grams of *p*-phenetylsulphinic acid were suspended in very dilute sulphuric acid solution, and warmed on the water-bath. About five drops of hydriodic acid (Zeisel) were then added, together with sufficient sulphurous acid to decolorise the solution. After about two hours, the mixture was rendered alkaline with sodium carbonate, and cooled. The disulphoxide formed solidified at once, and was collected and recrystallised from alcohol. In addition to the superior cleanliness of the crude product, the yield of disulphoxide by this method is greatly improved, being nearly that demanded by the equation:



Di-p-phenetyl disulphoxide forms handsome, colourless or faintly yellow tablets, melting at 89° *:

0.1434 gave 0.2949 CO_2 and 0.0726 H_2O . C=56.08; H=5.62.

$\text{C}_{16}\text{H}_{18}\text{O}_4\text{S}_2$ requires C=56.80; H=5.33 per cent.

* This melting point was erroneously given (Part I., *loc. cit.*) as 139° .

It was further characterised by reduction with a few drops of hydriodic acid (Zeisel) in glacial acetic acid in presence of sulphurous acid (Hinsberg, *loc. cit.*), when di-*p*-phenetyl disulphide, crystallising in white prisms, and melting at 48°, was produced. (Found, C=62·30; H=5·96. Calc., C=62·75; H=5·88 per cent.)

It may be observed in passing, that the same reagent, hydriodic acid free from iodine, which converts a sulphinic acid into disulphoxide so readily in aqueous solution, reduces the latter compound to disulphide in glacial acetic acid. This somewhat curious fact, together with some experiments on the mechanism of the conversion of sulphuric acids to disulphoxides, will, it is hoped, form the subject of a future communication.

The disulphoxide dissolved in concentrated sulphuric acid to a deep greenish-brown solution, which underwent no further change in colour. On pouring into water and recrystallising from alcohol, the compound was found to have been recovered unchanged (m. p. 85—86°. Found, C=56·39; H=5·36).

Condensation of Di-p-phenetyl Disulphoxide with Phenetole.

On adding phenetole to a solution of the disulphoxide in sulphuric acid, the colour turned to deep brown, and finally, by repeated addition of phenetole, it became faintly red or purple. Much sulphur dioxide was evolved in the course of the reaction. The aqueous acid solution obtained on pouring the mixture into cold water was converted into carbonate as described above, and a portion of it further converted into platinichloride.

The ethereal extract from the crude sulphonium sulphates in water left, on evaporation, a small amount of an oil, with the characteristic odour of an aromatic sulphide. On oxidation with potassium permanganate this yielded a crystalline compound, which melted at 160°; di-*p*-phenetylsulphone melts at 162—163° (Smiles and Le Rossignol, *loc. cit.*).

The crude platinum salt was purified in the usual manner from a mixture of alcohol and epichlorohydrin, when buff-coloured tablets separated, which appeared as a crystalline powder on drying at 100°. The compound melted at 200°, and, when mixed with an equal quantity of triphenetylsulphonium platinichloride, at 203—205°. It was accordingly triphenetylsulphonium platinichloride. (Found, C=47·65; H=4·59; Pt=16·27. Calc., C=48·08; H=4·51; Pt=16·28 per cent.)

The alcohol-epichlorohydrin mother liquor contained a very small quantity of an amorphous platinum salt of low melting point, which was not closely examined.

Another portion of the sulphonium carbonate solution was poured

into aqueous potassium dichromate. A bright orange-coloured dichromate resulted, which melted indefinitely at about 65° , and rapidly decomposed in presence of air:

0.1275 gave 0.0202 Cr_2O_3 . $\text{Cr}=10.84$.

$\text{C}_{48}\text{H}_{54}\text{O}_{18}\text{S}_2\text{Cr}_2$ requires $\text{Cr}=10.32$ per cent.

Triphenetylsulphonium dichromate was also prepared from a sample of the sulphonium chloride, and agreed in its properties with the above compound. (Found, $\text{Cr}=10.97$.)

Attempted Preparation of Di-o-carboxyphenyl Disulphoxide.

Attempts were made to oxidise di-*o*-carboxyphenyl disulphide by the following reagents: solid potassium permanganate in cold and in boiling acetic acid, hydrogen dioxide in hot acetic acid, and solid potassium permanganate in acetone; but without success. Similarly, *o*-carboxybenzenesulphinic acid did not give the desired product, either by the hydriodic acid method, or when heated with water at 130° . Finally, the oxidation of di-*o*-carbethoxyphenyl disulphide by hydrogen dioxide in acetone was tried, but again without success.

The ethyl ester was obtained by boiling the acid chloride with alcohol for an hour; the latter compound was prepared from the free acid and boiling thionyl chloride in slight excess, and crystallised from acetone in small prisms, melting at 152° (List and Stein, *Ber.*, 1898, **31**, 1670, using the phosphorus pentachloride method, obtained a sample melting at 135°). (Found, $\text{C}=48.60$; $\text{H}=2.63$. Calc., $\text{S}=48.99$; $\text{H}=2.33$ per cent.)

The diethyl ester melted at 118° (Found, $\text{C}=59.34$; $\text{H}=5.56$. Calc., $\text{C}=59.65$; $\text{H}=4.97$ per cent.), and after recovering it from treatment with hydrogen dioxide, it again melted at 118° . (Found, $\text{C}=59.74$; $\text{H}=4.99$.)

Di-p-tolyl Methyl Ether Disulphoxide.

Smiles and Le Rossignol (*loc. cit.*) have shown that the sulphination of *p*-tolyl methyl ether in presence of anhydrous aluminium chloride leads to formation of sulphoxide as the main product, but it has been found possible, by using light petroleum as a diluent, to increase the yield of the sulphinic acid (the first step in the sulphination process) to almost 50 per cent. of the starting material. It is interesting to record that the use of ether in place of light petroleum entirely stopped all sulphination; this was probably owing to the fact that the aluminium chloride combined with the ether instead of with the phenolic ether.

The sulphinic acid obtained by the use of light petroleum melted at 95—97°. (Found, C=51·44; H=4·94. Calc., C=51·62; H=5·38 per cent.) On attempting to convert it into the disulphoxide in the conventional way by heating with water at 130°, an uncrystallisable, brown oil was produced, but by the hydriodic acid method a solid product was formed, which separated from alcohol in pale yellow, soft prisms. *Di-p-tolyl methyl ether disulphoxide* melts at 83—86°:

0·1138 gave 0·2358 CO₂ and 0·0530 H₂O. C=56·53; H=5·18.

C₁₆H₁₈O₄S₂ requires C=56·80; H=5·33 per cent.

The substance was reduced by hydriodic acid in glacial acetic acid, with rather more difficulty than usual, to *di-p-tolyl methyl ether disulphide*, which crystallised from ether in soft tablets, melting at 73—74°:

0·0861 gave 0·1979 CO₂ and 0·0470 H₂O. C=62·69; H=6·07.

C₁₆H₁₈O₂S₂ requires C=62·75; H=5·88 per cent.

The disulphoxide dissolved in cold sulphuric acid with a deep greenish-black colour; the product obtained after pouring into water was a cream-coloured solid, readily soluble in alcohol, and crystallising therefrom in soft laminae, which contracted together at 160°, and melted at 184°. Analysis showed this compound to be a substance of the formula:

MeO·C₇H₆·S·C₇H₅(OMe)·SO·SO·C₇H₅(OMe)·SO·C₇H₆·OMe:

0·1313 gave 0·2808 CO₂ and 0·0660 H₂O. C=58·31; H=5·58.

C₃₂H₃₄O₇S₄ requires C=58·35; H=5·17 per cent.

The addition of *p*-tolyl methyl ether to the solution of the disulphoxide in sulphuric acid produced no change in appearance, and, indeed, the same product as before was subsequently isolated (m. p. 184°. Found, C=57·79; H=5·32).

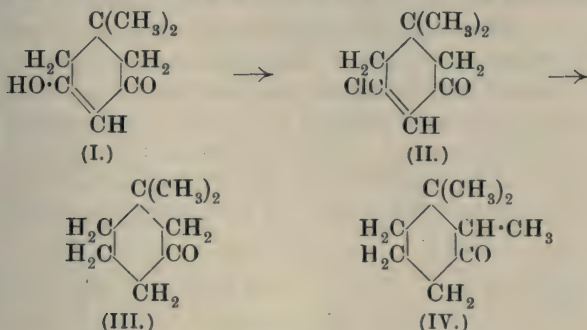
Moreover, this complex condensation product was submitted to reduction by hydriodic acid (free from iodine) in hot glacial acetic acid, but without result, the compound being recovered intact (m. p. 180—182°. Found, C=57·98; H=5·63).

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CXVII.—*Hydroaromatic Ketones. Part II. 1:1:2-Trimethylcyclohexan-3-one.*

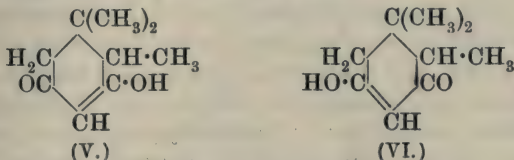
By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

IN 1907 (Trans., **91**, 63) the preparation of dimethylcyclohexanone (III) from dimethyldihydroresorcin (I) was described, the various steps being sufficiently explained by the following formulæ:



It seemed of interest to submit 1:1:2-trimethyldihydroresorcin to a similar series of reactions, so as to compare the properties and reactions of the resulting trimethylcyclohexanone (IV) with those of camphor, since these two ketones show a marked resemblance in the arrangement of the various groupings in their molecules. Further, it was thought that a more extended inquiry into the chemical behaviour of trimethyldihydroresorcin than has hitherto been carried out (Trans., 1901, **79**, 138) was desirable because, unlike dimethyldihydroresorcin (I), its molecule is not symmetrical, and consequently several new points of interest are raised.

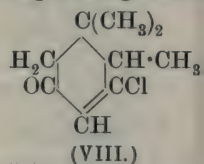
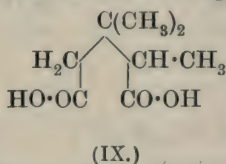
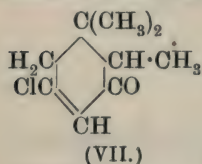
Some information as to the constitution of trimethyldihydroresorcin was afforded by a study of the products of its interaction with phosphorus pentachloride (Trans., 1906, **89**, 875), and from the experiments now described there can be no doubt that trimethyldihydroresorcin is a tautomeric substance, exhibiting the two forms represented by formulæ V and VI:



the particular form manifested depending on the nature of the

reagents with which the dihydroresorcin is brought in contact. For example, when treated with aniline, 97 per cent. of one individual anilide is obtained, but it cannot at present be said with which of the two forms of trimethyldihydroresorcin it corresponds. When hydrolysed, the anilide regenerates the original trimethyldihydroresorcin, which again is capable of behaving in either form, according to conditions of experiment. This point is at present being more thoroughly investigated, as it would, on theoretical grounds, appear possible for trimethyldihydroresorcin to exist in a still larger number of isomeric forms than indicated above.

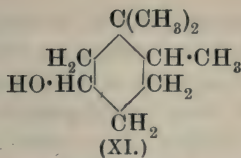
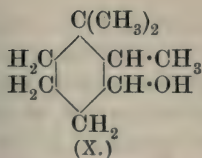
When 1:1:2-trimethyldihydroresorcin is treated with phosphorus trichloride, it gives chlorotrimethylcyclohexenone as a perfectly constant boiling liquid; it is nevertheless not homogeneous, but consists, for the most part, of 5-chloro-1:1:2-trimethyl- Δ^4 -cyclohexen-3-one (VII) mixed with 3-chloro-1:1:2-trimethyl- Δ^3 -cyclohexen-5-one (VIII), as proved by the record of experiments contained in the context. When oxidised with potassium permanganate,



the mixture of chloro-ketones gives $\alpha\beta\beta$ -trimethylglutaric acid (IX), but this information is of no value on constitutional grounds, apart from being a confirmation of the structure of trimethyldihydroresorcin, because this same substituted glutaric acid would result from the oxidation of either form of chlorotrimethylcyclohexenone.

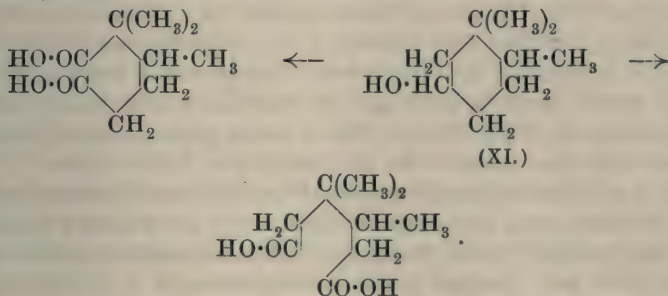
In the case of chlorodimethylcyclohexenone (*loc. cit.*), it was found possible directly to prepare dimethylcyclohexanone by the action of zinc dust and glacial acetic acid. This method was first tried with chlorotrimethylcyclohexenone, but it naturally gave rise to a mixture of trimethylcyclohexan-3-one and trimethylcyclohexan-5-one, mentioned later, which mixture it was not found possible to separate. The method of obtaining pure 1:1:2-trimethylcyclohexan-3-one is as follows, and differs somewhat from that employed in the preparation of 1:1-dimethylcyclohexan-3-one (*loc. cit.*).

If the mixture of chloro-ketones is reduced with sodium in moist ethereal solution, as in the case of chlorodimethylcyclohexenone (Trans., 1907, 91, 70), trimethylcyclohexanol is formed, but again this substance is not homogeneous, but consists of a mixture of the two possibilities, namely, 1:1:2-trimethylcyclohexan-3-ol (X) and 1:1:2-trimethylcyclohexan-5-ol (XI), in which the former largely predominates:

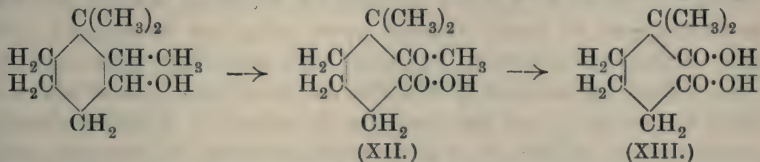


On treatment with benzoyl chloride, a solid and a liquid benzoyl derivative are obtained, and the former is proved by the following facts to be the benzoyl derivative of 1:1:2-trimethylcyclohexan-3-ol.

The alcohol regenerated from this solid benzoyl derivative gives, on oxidation with chromic acid mixture, the corresponding ketone in almost quantitative yield and in pure condition, the semicarbazone of which melts at 206° . Both the alcohol and this ketone gave a ketonic acid, $\text{C}_9\text{H}_{16}\text{O}_3$, when oxidised with potassium permanganate. Now 1:1:2-trimethylcyclohexan-5-ol (XI) could not, under these conditions, give a ketonic acid, but would yield a trimethyladipic acid:



On the other hand, 1:1:2-trimethylcyclohexan-3-ol (X) would be expected to give rise to δ -acetyl- δ -methylhexoic acid, $\text{C}_9\text{H}_{16}\text{O}_3$ (XII), which, on further oxidation, should give $\alpha\alpha$ -dimethyladipic



acid (XIII), and the latter product is readily obtained by oxidising the ketonic acid, $\text{C}_9\text{H}_{16}\text{O}_3$, with sodium hypobromite.

The constitution of the original alcohol is thus definitely established, and the argument may be equally well used as a proof of the constitution of the ketonic acid, $\text{C}_9\text{H}_{16}\text{O}_3$, for no other possibility exists when the structure of the substances from which it is derived is considered.

It would appear from the foregoing remarks that the liquid

benzoyl derivative *A* is the benzoyl derivative of 1:1:2-trimethylcyclohexan-5-ol, containing dissolved in it small amounts of the benzoyl derivative of 1:1:2-trimethylcyclohexan-3-ol, but so far it has not been found possible to isolate the former, or its corresponding alcohol, in a pure state. The question is, of course, complicated by the fact that both 1:1:2-trimethylcyclohexan-3-ol and 1:1:2-trimethylcyclohexan-5-ol can exist in *cis*- and *trans*-modifications, and it would appear that the benzoyl derivatives of all four possibilities are contained in the original mixture prepared by the action of benzoyl chloride on the alcohols.

In order to obtain evidence on this point, many experiments have been carried out, details of which will be given in a subsequent communication, when more definite information is forthcoming. The following is a brief summary.

In the first place, only two chlorotrimethylcyclohexenones (VII and VIII) can result from the action of phosphorus trichloride on trimethyldihydroresorcin, and from them there can only be formed two trimethylcyclohexanols, each capable of exhibiting *cis-trans*-isomerism. Further, two ketones, 1:1:2-trimethylcyclohexan-3-one and 1:1:2-trimethylcyclohexan-5-one, should result from oxidation of the mixed alcohols, each pair of stereoisomerides giving rise to one ketone, and it was thought that it might prove easier to separate these two ketones rather than the mixture of four alcohols.

The crude product resulting from the reduction of chlorotrimethylcyclohexenone was therefore oxidised with Beckmann's mixture, and the resulting liquid treated with semicarbazide acetate, when 75 per cent. was obtained as the semicarbazone of 1:1:2-trimethylcyclohexan-3-one (m. p. 206°). The remaining 25 per cent. melted at 170 — 185° , and no amount of fractional crystallisation would separate a constant melting substance from this material. Two ketones are certainly present, although it might be argued that the semicarbazone of lower melting point does not correspond with 1:1:2-trimethylcyclohexan-5-one, but with some other ketonic oxidation product formed under the influence of the chromic acid mixture. Such is, however, not the case, for if pure 1:1:2-trimethylcyclohexan-3-ol be oxidised with Beckmann's mixture, it gives, in quantitative yield, 1:1:2-trimethylcyclohexan-3-one; and, further, if the crude ketones produced by oxidising the mixture of alcohols be again reduced, the original mixture of alcohols is formed, no evidence of the slightest trace of any other substance being obtained.

As the attempts to separate the ketones did not give satisfactory results, attention was then directed to the mixture of alcohols, and, in the first place, benzoyl chloride was tried; but only the solid benzoyl derivative of *trans*-1:1:2-trimethylcyclohexan-3-ol (without

having any definite proof to offer, this modification is named *trans* from analogy to other known reactions of similar type) was obtained in a pure condition. The alcohols regenerated from the benzoyl derivatives, from which the above-mentioned solid had separated, were treated with *o*-nitrobenzoyl chloride, when considerable quantities of the *o*-nitrobenzoyl derivative of 1:1:2-trimethylcyclohexan-3-ol, melting at 114°, were isolated, together with material of lower melting point (m. p. 75—78°). After repeated fractional crystallisation of the latter, a portion was isolated, melting sharply at 77—78°, and having all the appearances of an individual substance. It was hydrolysed, and the resulting alcohol converted into the corresponding ketone. This was treated with semicarbazide acetate, when 25 per cent. of the ketone was obtained as the semicarbazone of 1:1:2-trimethylcyclohexan-3-one, melting at 206°. Moreover, on oxidation the ketone gave δ -acetyl- δ -methylhexoic acid in amount corresponding with 30—35 per cent. of the ketone. It seems hardly probable that the substance melting at 77—78° could contain 30—35 per cent. of the nitrobenzoyl derivative of *trans*-1:1:2-trimethylcyclohexan-3-ol, melting at 114°, but as the *cis*-modification of this alcohol would also give 1:1:2-trimethylcyclohexan-3-one on oxidation, the obvious conclusion is that the nitrobenzoyl derivative melting at 77—78° consisted of the *cis*-form of 1:1:2-trimethylcyclohexan-3-ol and both the *cis*- and *trans*-modifications of 1:1:2-trimethylcyclohexan-5-ol.

The somewhat complicated question of the constitution of trimethyldihydroresorcin is at present being more fully studied.

EXPERIMENTAL.

1 : 1 : 2-Trimethyldihydroresorcin was prepared as already described (Trans., 1901, **79**, 141), except that the crude product was crystallised from water, instead of from a mixture of chloroform and light petroleum. In crystallising from water, it is essential that the following conditions should be observed. The resorcin is suspended in seven times its weight of water, the whole heated to boiling, filtered, and the residue extracted again five times with similar amounts of water, when all but a slight, sticky residue is dissolved. On cooling, the solutions turn cloudy, when the resorcin commences to crystallise out in radiating clusters of transparent needles, melting at 99·5—100°.

In the previous description of the preparation of trimethyldihydroresorcin (*loc. cit.*, p. 143), it was mentioned that on acidifying the solution obtained by hydrolysing ethyl trimethyldihydroresorcyrate with potassium hydroxide, a small amount of material separated, which was insoluble in water and ether, and probably

consisted of 1:1:2-trimethyldihydroresorcin-3-carboxylic acid. In preparing larger quantities of trimethyldihydroresorcin it was observed that if the solution was acidified while still warm and then allowed to remain with frequent shaking, none of this acid was produced; but, on the other hand, if the solution was kept cold during acidification, large quantities separated. This material could not be purified by crystallisation, as on warming slightly carbon dioxide was evolved and trimethyldihydroresorcin formed. It was therefore well washed with water, acetone, and ether, and dried in a vacuum, when it melted sharply at 116° , with vigorous evolution of gas. The following analysis, in conjunction with the above data, confirm the suspicion that this substance is trimethyldihydroresorcincarboxylic acid:

0.2096 required 21.6 c.c. $N/10$ -KOH. M.W. = 194.

$C_{10}H_{14}O_4$ requires M.W. = 198.

The *anilide* of trimethyldihydroresorcin was prepared by heating 4 grams of the substance with 3 grams of freshly distilled aniline in dry benzene solution for ten hours on a water-bath. On cooling, 3.9 grams, m. p. 159 — 160° , separated, and by addition of light petroleum (b. p. 40 — 60°) a further 1.7 grams were obtained; or, in all, 5.6 grams, where theory requires 5.9 grams. The anilide crystallises from ethyl acetate in white, flattened, nacreous needles, melting at 160° :

Found: N = 5.82. $C_{15}H_{19}ON$ requires N = 6.11 per cent.

It is not hydrolysed by boiling for twelve hours with alcoholic potassium hydroxide, but when heated with a mixture of two parts of concentrated hydrochloric acid and one part of water it gave a theoretical yield of trimethyldihydroresorcin, melting at 99 — 100° .

Action of Phosphorus Trichloride on Trimethyldihydroresorcin.

Chlorotrimethylcyclohexenone was prepared by the method already described in the case of chlorodimethylcyclohexenone (Trans., 1903, **83**, 117), except that the heating with phosphorus trichloride was continued for three hours instead of two and a-half hours. The residue after distillation gave the following analytical results:

0.1046 gave 0.2390 CO_2 and 0.0702 H_2O . C = 62.33; H = 7.45.

0.2088 „ 0.1765 AgCl. Cl = 20.91.

$C_9H_{13}OCl$ requires C = 62.61; H = 7.53; Cl = 20.58 per cent.

Chlorotrimethylcyclohexenone, the yield of which is 64—66 per cent. of the theoretical amount, is a colourless, highly refractive liquid, boiling at $130^{\circ}/42$ mm., and possessing a marked odour of camphor. It is insoluble in cold potassium hydroxide solution, but on boiling is slowly dissolved, being converted into trimethyl-

dihydroresorcin; a change which is also brought about by dissolving the chloro-ketone in glacial acetic acid saturated with hydrogen bromide, and allowing the whole to stand.

The *semicarbazone* prepared in the usual manner is insoluble in light petroleum (b. p. 60—80°), readily soluble on warming in acetone, chloroform, benzene, or ethyl alcohol, and crystallises from the latter solvent in minute plates, melting and decomposing at 185—186°:

Found: N=18·26. $C_{10}H_{16}ON_3Cl$ requires N=18·30 per cent.

The *oxime* was prepared by dissolving one molecule of the chloro-ketone in absolute alcohol, adding two molecules of dry, powdered hydroxylamine hydrochloride, three molecules of dry, powdered potassium acetate, and allowing to remain for three days. The whole was then heated to the boiling point of the alcohol, filtered, washed with a little hot alcohol, the filtrate evaporated to a small volume, and then diluted with water, when colourless, needle-shaped crystals separated, which were purified by crystallisation from alcohol:

Found: N=7·34. $C_9H_{14}ONCl$ requires N=7·46 per cent.

The oxime is readily soluble in benzene and chloroform, somewhat less soluble in ethyl alcohol, ethyl acetate, or acetone, and crystallises from light petroleum (b. p. 60—80°), or, better, from aqueous ethyl alcohol, in long, colourless, transparent needles, melting at 121°, with slight evolution of gas, to a colourless liquid, which then decomposes.

Oxidation of Chlorotrimethylcyclohexenone.—Ten grams of the chloro-ketone were suspended in 250 c.c. of water, and a 4 per cent. solution of potassium permanganate slowly added until no longer decolorised. As oxidation took place fairly rapidly, the solution was cooled by the addition of small quantities of ice, and then worked up in the usual manner. The resulting colourless, oily liquid (10 grams) was treated with an alcoholic solution of semicarbazide acetate, when it yielded 1·5 grams of a white solid, neutral to litmus, and practically insoluble in the ordinary organic solvents. After crystallisation from hot water, in which liquid it is not at all readily soluble, small, colourless, transparent plates were obtained. These melted at 245°, and contained 46·9 per cent. of nitrogen, but the amount was too small to permit of a thorough investigation being made.

The liquid from which the above solid had separated was distilled in steam, to remove alcohol, the residue evaporated to a small bulk, acidified with hydrochloric acid, and extracted ten times with ether. The oil obtained on evaporation of the ether partly solidified, and after spreading on porous plate gave 4·6 grams of a solid, separating

from a mixture of chloroform and light petroleum (b. p. 40—60°) in transparent plates, melting at 85—86°; nor was this melting point lowered on mixing with pure $\alpha\beta\beta$ -trimethylglutaric acid. The identity of this substance was further proved by converting a portion into the anhydride, which crystallised from light petroleum (b. p. 80—100°) in radiating clusters of long, transparent, fern-like crystals, melting at 87—88°. When treated with aniline in benzene solution, the anhydride gave an anilic acid, melting at 150°. Perkin and Thorpe (Trans., 1899, **75**, 65) give the melting point of $\alpha\beta\beta$ -trimethylglutaric acid as 88°, but the present authors have not been able to obtain the melting point higher than 85—86°, even after repeated crystallisation from different solvents, such as water, hydrochloric acid, or preferably a mixture of chloroform and light petroleum (b. p. 40—60°). Moreover, this same melting point was obtained by dissolving the pure anhydride in water, and allowing to crystallise.

Perkin and Thorpe give the melting point of the anhydride crystallised from a mixture of ethyl acetate and light petroleum at 82°; the best solvent is, however, light petroleum (b. p. 80—100°), when the anhydride is obtained, melting sharply at 87—88°, that is, slightly higher than the acid.

Trimethyldihydroresorcin anhydride was obtained similarly to dimethyldihydroresorcin anhydride (Trans., 1903, **83**, 119), as a residue on distilling chlorotrimethylcyclohexenone. This was triturated with ether, when it gave a clean, white solid, which was purified by crystallisation from ethyl acetate:

0.1260 gave 0.3425 CO₂ and 0.1023 H₂O. C=74.13; H=9.02.

C₁₈H₂₆O₃ requires C=74.48; H=8.96 per cent.

The anhydride is readily soluble in acetone and chloroform in the cold, somewhat less so in benzene, and crystallises from ethyl alcohol or ethyl acetate in transparent needles, melting at 158—159°.

Reduction of Chlorotrimethylcyclohexenone with Sodium in Moist Ethereal Solution.

Quantities of chlorotrimethylcyclohexenone were reduced exactly as described for the reduction of chlorodimethylcyclohexenone (Trans., 1905, **87**, 1494; 1907, **91**, 70), except that three times, instead of twice, the calculated quantity of sodium was used. Further, the crude product was distilled in steam, which separates the non-volatile resinous by-product, before being distilled under diminished pressure:

0.1847 gave 0.5134 CO₂ and 0.2084 H₂O. C=75.81; H=12.53.

C₉H₁₈O requires C=76.05; H=12.67 per cent.

Trimethylcyclohexanol, the yield of which is 56—60 per cent. of the theoretical amount, is a viscid, colourless, refractive liquid, boiling at $101^{\circ}/19$ mm., and possessing a marked camphoraceous odour. It does not absorb bromine in chloroform solution, and only partly solidifies when cooled in a mixture of ice and hydrochloric acid. On dissolving in alcohol and treating with concentrated sulphuric acid, it gives an orange colour, turning to orange-red.

Action of Benzoyl Chloride on Trimethylcyclohexanol.

Trimethylcyclohexanol, in quantities of 20 grams at one time, was treated with benzoyl chloride as previously described (Trans., 1907, **91**, 72). The resulting product (34.5 grams) was spread on porous plate (plate=A), when 17 grams of a white solid remained, which, after one crystallisation from aqueous alcohol, melted sharply at 61° :

0.1822 gave 0.5190 CO_2 and 0.1475 H_2O . $\text{C}=77.68$; $\text{H}=8.99$.

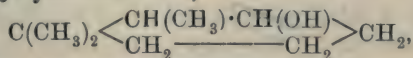
$\text{C}_{16}\text{H}_{22}\text{O}_2$ requires $\text{C}=78.04$; $\text{H}=8.94$ per cent.

The *benzoyl* derivative of 1:1:2-trimethylcyclohexan-3-ol is readily soluble in the cold in the usual organic solvents, and crystallises from aqueous alcohol in long, transparent, glistening needles, melting at 61° , and possessing a slight odour, somewhat resembling that of ethyl benzoate. When hydrolysed with alcoholic potassium hydroxide, an oil was obtained, which distilled quite constantly at $97^{\circ}/19$ mm., and immediately solidified to a mass of long, colourless, transparent needles:

0.1033 gave 0.2869 CO_2 and 0.1178 H_2O . $\text{C}=75.75$; $\text{H}=12.67$.

$\text{C}_9\text{H}_{18}\text{O}$ requires $\text{C}=76.05$; $\text{H}=12.67$ per cent.

1:1:2-Trimethylcyclohexan-3-ol,



obtained in theoretical amount by the above hydrolysis, melts at 28° , possesses a camphoraceous odour, and is extremely soluble in the cold in the usual organic solvents. It does not absorb bromine in chloroform solution, and when treated with alcoholic sulphuric acid gives only a very faint yellow colour.

The *m*-nitrobenzoyl derivative was prepared by the action of *m*-nitrobenzoyl chloride under similar conditions to those employed for the preparation of the benzoyl derivative. It is readily soluble in the ordinary organic solvents, and crystallises from aqueous alcohol in colourless, nacreous, scaly needles, melting at 44° :

Found: $\text{N}=4.80$. $\text{C}_{16}\text{H}_{21}\text{O}_4\text{N}$ requires $\text{N}=4.81$ per cent.

The *o*-nitrobenzoyl derivative prepared in a similar manner is readily soluble in chloroform or benzene, less soluble in acetone

or ethyl acetate, and crystallises from alcohol in stout, faintly yellow needles, melting at 114° :

Found: $N=4.78$. $C_{16}H_{21}O_4N$ requires $N=4.81$ per cent.

Oxidation of 1:1:2-Trimethylcyclohexan-3-ol:—Five grams of the alcohol were oxidised with potassium permanganate in the usual manner. The resulting oil yielded 3.5 grams of a semicarbazone on treatment with semicarbazide acetate, which melted at 169° , and was proved to be identical with the semicarbazone of δ -acetyl- δ -methylhexoic acid, described on p. 1111.

Preparation of 1:1:2-Trimethylcyclohexan-3-one.

Quantities of 1:1:2-trimethylcyclohexan-3-ol were oxidised by adding 10 grams of the alcohol to 94 grams of Beckmann's chromic acid mixture, keeping the whole well shaken. The temperature gradually rose, and at 50 – 60° a reaction set in, which was very soon complete. The mixture was then heated on the water-bath at 50 – 55° for half an hour, with constant shaking, extracted with ether, the ethereal solution washed with potassium hydroxide solution, then with water, dried over calcium chloride, and the residue obtained on evaporation of the ether distilled in air, when the whole passed over at 190.5 – 191° :

0.1841 gave 0.5194 CO_2 and 0.1910 H_2O . $C=76.94$; $H=11.53$.

$C_9H_{16}O$ requires $C=77.14$; $H=11.43$ per cent.

1:1:2-Trimethylcyclohexan-3-one, $C(CH_3)_2 \begin{matrix} \text{CH}(CH_3) \cdot CO \\ \text{CH}_2 \text{---} \text{CH}_2 \end{matrix} CH_2$, is a clear, colourless, refractive liquid, boiling at 190.5 – $191^{\circ}/750$ mm., and having a sp. gr. of 0.9213 at $15^{\circ}/15^{\circ}$. It possesses a very strong camphoraceous odour, and with alcoholic sulphuric acid gives only a faint yellow colour. When dissolved in chloroform and a solution of bromine in the same solvent added, no bromine is absorbed for some time; then the colour suddenly disappears, when on adding more bromine it is rapidly absorbed, and torrents of hydrogen bromide are given off (compare Trans., 1907, 91, 81). The yield of ketone is quantitative.

The *semicarbazone*, prepared in the usual manner, is very slightly soluble in ethyl acetate, acetone, benzene, or chloroform, and crystallises from alcohol in small, colourless, nacreous scales, melting at 206° with evolution of gas:

Found: $N=21.29$. $C_{10}H_{19}ON_3$ requires $N=21.32$ per cent.

The *oxime* is readily soluble in the usual organic solvents. It crystallises from light petroleum (b. p. 40 – 60°) or aqueous alcohol in stout, colourless, transparent needles, melting at 95° , and possessing a marked and sickly camphoraceous odour:

Found: N=9.07. $C_9H_{17}ON$ requires N=9.03 per cent.

Oxidation of the Ketone:—Eleven grams of the ketone were suspended in 250 c.c. of water, a 4 per cent. solution of potassium permanganate gradually added, and the whole continuously shaken on a shaking machine. Oxidation took place very slowly, requiring sixty-four hours for completion, when 650 c.c. of potassium permanganate solution had been used. The product was worked up in the usual manner, and yielded 13.8 grams of an almost colourless oil, which on treatment with an alcoholic solution of semicarbazide acetate gave 15 grams of a white solid, which, after one crystallisation from ethyl alcohol, was analysed:

0.1235 gave 19.6 c.c. N_2 (moist) at 14° and 745 mm. N=18.31.

$C_{10}H_{19}O_3N_3$ requires N=18.34 per cent.

The *semicarbazone* of δ -acetyl- δ -methylhexoic acid is only very slightly soluble in ethyl acetate, acetone, chloroform, or benzene, somewhat more so in methyl or ethyl alcohols, and crystallises from the latter solvent in radiating clusters of short, transparent, flattened needles, melting at 169° , with evolution of gas. When hydrolysed by heating with diluted hydrochloric acid for one hour on the water-bath, an oil was obtained which distilled quite constantly at $188.5^\circ/26$ mm., the yield being quantitative:

0.1881 gave 0.4320 CO_2 and 0.1595 H_2O . C=62.63; H=9.42.

$C_9H_{16}O_3$ requires C=62.79; H=9.30 per cent.

δ -Acetyl- δ -methylhexoic acid, $CH_3 \cdot CO \cdot C(CH_3)_2 \cdot [CH_2]_3 \cdot CO_2H$, is a colourless, viscid liquid, boiling at $188.5^\circ/26$ mm. It does not solidify when cooled to -10° , and is very slightly soluble in cold water, and not readily so in boiling water.

The *silver* salt, prepared in the usual manner, is a white, curdy, insoluble precipitate:

0.2410 gave 0.0936 Ag. Ag=38.83.

$C_9H_{15}O_3Ag$ requires Ag=38.71 per cent.

The *oxime*, prepared exactly as described on p. 1107, is readily soluble in the usual organic solvents excepting light petroleum, and crystallises from water in colourless, slender needles, melting at $104-105^\circ$:

Found: N=7.37. $C_9H_{17}O_3N$ requires N=7.49 per cent.

When crystallised from benzene, radiating clusters of glistening, flaky needles were obtained, which melted at $92-93^\circ$, but did not become clear until 95° . The crystals contain half a molecule of benzene of crystallisation, which they do not lose on drying in a vacuum:

Found: N=6.15. $(C_9H_{17}O_3N)_2 \cdot C_6H_6$ requires N=6.17 per cent.

On boiling this substance with water, a marked odour of benzene was observed, and, on cooling, slender needles separated, which melted sharply at 104—105°, and were identical with the original oxime.

Oxidation of δ -Acetyl- δ -methylhexoic Acid:—Two grams of the ketonic acid were suspended in water, a slight excess of sodium hydroxide added, then bromine drop by drop, the whole being maintained sufficiently alkaline to remain colourless. On completion of the reaction, the solution, after separation of the bromoform, was treated with sodium bisulphite to destroy excess of hypobromite, acidified with dilute sulphuric acid, saturated with ammonium sulphate, and extracted ten times with ether. The ethereal solution, after drying, yielded two grams of a white solid, which crystallised from a mixture of benzene and light petroleum (b. p. 40—60°) in radiating clusters of slender needles, melting at 89—90°; nor was this melting point lowered on mixing with pure *aa*-dimethyladipic acid. (Found, C=55·09; H=8·00. Calc., C=55·17; H=8·04 per cent.)

Reduction of 1:1:2-Trimethylcyclohexan-3-one:—Ten grams of the ketone were reduced with sodium in moist ethereal solution, as previously described (Trans., 1905, **87**, 1494; 1907, **91**, 70). The resulting 10 grams of liquid distilled constantly at 96·5°/18 mm., gave the same colour reaction with alcoholic sulphuric acid as pure 1:1:2-trimethylcyclohexan-3-ol, but did not solidify quite so readily or completely. Eight and a-half grams were therefore treated with *o*-nitrobenzoyl chloride in the usual manner, when there were obtained 14·8 grams of the *o*-nitrobenzoyl derivative melting at 114° (compare p. 1110), and 0·4 gram of a mixture melting at 94—95°, and not clarifying until 98°. This proves that if during the reduction of the ketone both the *cis*- and *trans*-forms of the alcohol are produced, one of the forms is present only in very minute quantities.

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CXVIII.—*Electrolytic Reduction. Part IV.*
Aromatic Aldehydes.

By HERBERT DRAKE LAW.

A PREVIOUS study of the electrolytic reduction products of the aromatic aldehydes has shown that a very small change of constitution exercises a relatively large influence on the course of the reaction. The variation, however, appears to be governed in a definite manner, and in the case of the compounds investigated the influence of the configuration has been similar in all cases. The scope of the work has been limited to a small group of aldehydes, and it appeared desirable to extend the field of observation before attempting a generalisation. The monochlorobenzaldehydes were therefore prepared and reduced, and the results compared with those already described (Trans., 1907, **91**, 748). The *o*- and *m*-substituted benzaldehydes yielded products of a resinous nature as before, whilst *p*-chlorobenzaldehyde gave well defined, crystalline compounds, and confirmed previous experience (*loc. cit.*).

The configuration of the aldehydes is not the only factor influencing the course of these reactions, and it has been shown that the nature of the electrolyte plays an important part. The reduction product differs according as the solvent medium is acid or alkaline, and, for further comparison, an attempt was made to produce an electrolytic mixture that would remain neutral throughout an experiment. This endeavour was unsuccessful, but a compromise was effected in the following manner: A solvent composed of water, ethyl acetate, and alcohol was used, and potassium acetate was employed as electrolyte. The free alkali then generated during the normal course of electrolysis in a divided cell could not accumulate, but was utilised in hydrolysing the ethyl acetate of the solvent, forming alcohol and potassium acetate. Another series of experiments was conducted under these new conditions. The chief difference in the results was a marked decrease in the amount of resinous matter produced during the reduction, and many compounds which had hitherto yielded no crystalline substances gave a product easy of identification. It was hoped, therefore, that experiments conducted with this new solvent would yield results showing the influence of structural differences with greater precision than those previously obtained.

EXPERIMENTAL.

The following experiments with the three monochlorobenzaldehydes were conducted in the apparatus already described (Trans.,

1906, **89**, 1512). The solvent was composed of 60 c.c. of alcohol and 20 c.c. of water. The electrolyte was 5 per cent. of potassium hydroxide or sulphuric acid, according as an alkaline or an acid medium was desired. Another series of experiments was conducted in a mixture of 20 c.c. of ethyl acetate, 30 c.c. of alcohol, 20 c.c. of water, and 5 per cent. of potassium acetate. The latter mixture will be referred to later as the "nearly neutral solvent." Five grams of aldehyde were reduced at one time. A current of 1 ampere was employed for three to four hours, the current density being 0.05 ampere per square decimeter. An apparatus containing five times the above quantities was also used, but the other conditions of the experiments were not altered. The material of the cathodes was composed of pure commercial sheet metal cut to the desired size and shape. The thickness of the metal varied from 1 to 2 mm., except in those cases where platinum was employed. In the latter experiments stout platinum foil was used. A new cathode was used for each experiment, the metal being cleaned with hot nitric acid immediately before the reduction was commenced.

p-Chlorobenzaldehyde.

The product of reduction of *p*-chlorobenzaldehyde contained *p*-chlorotoluene, *p*-chlorobenzyl alcohol, *p*-chlorohydrobenzoin, resinous matter, unchanged material, and small quantities of other substances. The results obtained under varying conditions are given below.

Cathode material	Copper	Copper	Nickel	Platinum (smooth)	Lead
Supertension of the cathode	0.6 volt		0.66 volt	0.56 volt	0.9 volt
Condition of solvent	alkaline	acid	alkaline	alkaline	alkaline
<i>p</i> -Chlorotoluene	0.0 %	12.5 %	0.0 %	0.0 %	0.0 %
<i>p</i> -Chlorobenzyl alcohol	0.0	17.0	small	0.0	33.0
<i>p</i> -Chlorohydrobenzoin.....	75.0	50.0	65.0	50.0	33.0
Unchanged aldehyde	25.0	20.0	30.0	35.0	20.0
Resinous matter	small	small	small	small	small

The following method was used to separate the above products: The reaction mixture was first diluted with water, and left for some hours. The precipitated *p*-chlorohydrobenzoin was removed by filtration, and the oily residue extracted with ether. The ethereal extract was allowed to remain overnight in presence of a saturated aqueous solution of sodium hydrogen sulphite, when an insoluble compound was formed with the aldehyde, and removed by filtration. The ethereal layer was separated, washed, dried, and the ether finally evaporated. The residual oil partly solidified on cooling, depositing a further quantity of *p*-chlorohydrobenzoin, which was separated as before. The oil remaining was finally fractionated under diminished pressure, when *p*-chlorotoluene and *p*-chlorobenzyl

alcohol were obtained. The residue from this operation contained a further quantity of *p*-chlorohydrobenzoin and resinous matter. The amount of the former was estimated by converting it into *p*-chlorobenzil with concentrated nitric acid, and then crystallising from alcohol.

The *p*-chlorobenzyl alcohol was crystallised slowly from benzene, and obtained in large prisms, melting at 75°. (Found, C=58·98; H=5·28. Calc., C=58·94; H=4·91 per cent.) When crystallised rapidly from light petroleum it was deposited in fine needles, melting at 73°. The latter value agrees with that found by Mettlers (*Ber.*, 1905, **38**, 1750).

The *pp'*-dichlorohydrobenzoin was crystallised from benzene, and melted at 151°. When oxidised with nitric acid it formed *pp'*-dichlorobenzil, melting at 200°.

A small quantity of another substance, melting at 237°, was also obtained in some cases:

0·1057 gave 0·2041 CO₂ and 0·0313 H₂O. C=52·66; H=3·29.

C₁₄H₁₀Cl₄ requires C=52·50; H=3·12 per cent.

This compound thus appears to be *pp'*-dichlorostilbene dichloride. The compound dissolves in hot concentrated nitric acid, and on precipitating with water the substance obtained melts at 170—175°. No further experiments were conducted, as the amount of material available was very small.

m-Chlorobenzaldehyde.

m-Chlorobenzaldehyde, in both acid and alkaline solution, yielded a product which was entirely resinous, and the reduction was therefore conducted in the nearly neutral medium. The product now contained *m*-chlorobenzyl alcohol, *mm'*-dichlorohydrobenzoin, resinous matter, and unchanged aldehyde. This mixture was diluted with water, extracted with ether, the ether removed, and the resulting oil distilled in a current of steam. The distillate contained the unchanged aldehyde and *m*-chlorobenzyl alcohol, which were separated as before. The residue in the distillation flask was extracted with successive quantities of boiling water. The latter solution on cooling deposited needles, which were very sparingly soluble in water. These were recrystallised from hot water, and finally from light petroleum, and melted at 95°. Yield 35 per cent.:

0·1047 gave 0·2275 CO₂ and 0·0425 H₂O. C=59·26; H=4·51.

Found, M.W. (by cryoscopic method in benzene)=284 and 283.

C₁₄H₁₂O₂Cl₂ requires C=59·36; H=4·28 per cent. M.W.=283.

The substance therefore appeared to be *mm'*-dichlorohydrobenzoin. It could not be converted into the corresponding dichloro-

benzil with concentrated nitric acid. When oxidised with chromium trioxide in aqueous solution it yielded a mixture of *m*-chlorobenzoic acid (m. p. 153°) and *m*-chlorobenzaldehyde, the latter also being identified by the preparation of its semicarbazone (m. p. 228°).

o-Chlorobenzaldehyde.

The product of reduction of *o*-chlorobenzaldehyde in both acid and alkaline solution was entirely resinous, and as a consequence the nearly neutral solvent was tried. The reduced mixture was then treated in the manner previously described, and 25—30 per cent. of solid matter was obtained on distilling in a current of steam. The latter substance, after crystallising from light petroleum, melted at 74° and boiled at $225\text{--}226^{\circ}$, and in general properties appeared to be identical with *o*-chlorobenzyl alcohol. The residue in the distilling flask was wholly resinous.

Tolualdehydes.

It has been pointed out in a previous paper (*loc. cit.*) that *o*- and *m*-tolualdehydes, when reduced electrolytically, yielded products which were largely resinous. The reaction was therefore conducted in the nearly neutral medium, as already described, and the resulting mixture separated by the following modified process. The ethereal extract of the product was distilled, first under the ordinary pressure up to 200° , and then under diminished pressure. The separate fractions were then treated as described above.

o-Tolualdehyde.

The fraction boiling below 240° contained chiefly unchanged aldehyde (20 per cent.). There were also small quantities of both toluene and *o*-methylbenzyl alcohol present. The largest portion of the product boiled at $230\text{--}260^{\circ}/30$ mm., and yielded an oil which solidified on cooling (40 per cent.). This substance was washed with small quantities of light petroleum, crystallised from hot water several times, and finally from light petroleum. Colourless, crystalline needles were obtained, melting at 118° :

0.1009 gave 0.2945 CO_2 and 0.0690 H_2O . $\text{Cl}=79.60$; $\text{H}=7.59$.

$\text{C}_{16}\text{H}_{18}\text{O}_2$ requires $\text{C}=79.34$; $\text{H}=7.44$ per cent.

This substance therefore appeared to be *isohydrotoluoin*. An isomeric compound, which has been named *hydrotoluoin*, has already been obtained from *o*-tolualdehyde by electrolytic reduction (*loc. cit.*).

These two substances are probably the racemic and meso-forms of hydrotoluoïn. The constitution of the compound melting at 118° was confirmed by oxidising it with chromic acid in aqueous solution, when it yielded *o*-toluic acid (m. p. 102°) and *o*-tolualdehyde, the semicarbazone of which melted at 196 — 198° . It resinified when treated with nitric acid.

m-Tolualdehyde.

m-Tolualdehyde was reduced in the nearly neutral medium, and the product, when fractionally distilled, yielded the following three main fractions: (I) b. p. 120 — $150^{\circ}/760$ mm., 28 per cent.; (II) b. p. 170 — $220^{\circ}/760$ mm., 46 per cent.; (III) b. p. 200 — $240^{\circ}/30$ mm., 18 per cent. Fraction (I) consisted almost entirely of *m*-toluene. (II) was composed of two parts of *m*-methylbenzyl alcohol and one of unchanged aldehyde. (III) was a viscid oil, which did not crystallise on long keeping, and on further manipulation yielded no well defined compound. The residue in the distilling flask amounted to 8 per cent. of the total product.

The results obtained in the nearly neutral medium may be summarised in the following table:

Substance reduced	<i>m</i> -Chloro- benzaldehyde	<i>o</i> -Chlorobenz- aldehyde	<i>m</i> -Tolu- aldehyde	<i>o</i> -Tolu- aldehyde
Cathode material	copper	copper	copper	copper
Hydrocarbons produced	—	—	28 %	small quantity
Alcohols	5 %	25—30 %	30	—
Glycols.....	35	—	—	40 %
Unchanged aldehyde.....	20	20	16	20
Other products	—	—	18	—
Resins	40	50	8	30

It will be seen that the quantity of resinous matter increases as the substituted group in the aldehyde changes from the *m*- to the *o*-position.

In conclusion, I wish to express my thanks to the Government Grant Committee for partly defraying the cost of many of the products dealt with above.

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CXIX.—*The Conductivity and Viscosity of Aqueous Solutions of Aniline Hydrochloride at 25°.*

By NEVIL VINCENT SIDGWICK and BERNARD HOWELL WILSDON.

IN connexion with the work described in the succeeding paper, we were led to determine the dissociation of aqueous solutions of aniline hydrochloride between decinormal and normal; and as the results seemed to have some intrinsic interest, the measurements were afterwards extended to stronger solutions.

The conductivity of aniline hydrochloride has been measured by various chemists, but always in very dilute solution, the object being to determine either the velocity of the anilinium ion, or the strength of the base by means of the hydrolysis of the salt (compare Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 215; Walker, *ibid.* 1889, **4**, 335; Niementowski and Roszkowski, *ibid.*, 1897, **22**, 148; Lundén, *Med. från K. Vet. Nobelinstit.*, 1907, **1**, 7, 4). We have not been able to find any measurements of solutions even as strong as decinormal. These stronger solutions, however, have an important bearing on the question of the relation between conductivity and viscosity. A solution saturated at 25° is more than four times normal, and has a viscosity nearly four times that of water.

Conductivity at Infinite Dilution.

This must be determined in presence of excess of aniline, in order to eliminate hydrolysis. Bredig (*loc. cit.*) found that the conductivity was the same in presence of *N*/32- and *N*/64-aniline, and hence assumed that the latter quantity was sufficient to render the hydrolysis inappreciable. He obtained at 25° $\mu_{\infty} = 113.5$. Lundén (*loc. cit.*), in presence of excess of aniline, the amount of which is not stated, obtained $\mu_{\infty} = 112.3$.

Our measurements were carried out in a cell of low resistance, having the electrodes sealed on to the glass cap. The cell contained the aniline solution, and the salt solution was added from a weight-pipette (the purification of the materials is described below). The cell was standardised with potassium chloride solutions of several different strengths. Two series of measurements were made, one with *N*/58- and one with *N*/22-aniline. The resulting values of μ were plotted against the square root of the concentration, and in both series gave a straight line within 1 part in 1000, from which

the infinity value was obtained; the conductivity of the water, which is given in gemmhos, was subtracted. Temperature 25°.

I. Aniline $N/58$.
Water = 1.07 gemmhos.

V .	μ .
245.1	106.13
317.3	107.06
1377.0	110.51
∞	113.70

II. Aniline $N/22$.
Water = 1.20 gemmhos.

V .	μ .
191.4	104.15
478.0	107.22
680.3	108.06
1142.4	109.27
∞	112.70

These results show that a greater concentration of free aniline than was used by Bredig is necessary to eliminate hydrolysis completely. The value $\mu_{\infty} = 112.7$ was taken as correct.

Stronger Solutions: Viscosity and Conductivity.

The two properties were measured as far as possible with the same solutions. The aniline was purified by Hantzsch and Freese's method (*Ber.*, 1894, **27**, 2966). It was dried over solid potassium hydroxide, and twice distilled. It passed over within 1° as a colourless liquid, with a distinct blue fluorescence. The hydrochloride was purified by repeated crystallisation from water, and was dried in a vacuum over potassium hydroxide and sulphuric acid. Analysis with silver nitrate showed it to contain the theoretical percentage of chlorine.

The solutions were made up by weight (in water of 0.8 to 1.3 gemmhos conductivity at 25°), and their composition checked by gravimetric analysis with silver. The densities were determined in a pycnometer of about 15 c.c. capacity, and the viscosities in two Ostwald viscometers of about three minutes period with water. In nearly every case the same solution was measured in both viscometers, and the results agreed to 2 parts in 1000, which about represents the limit of accuracy of this type of viscometer.

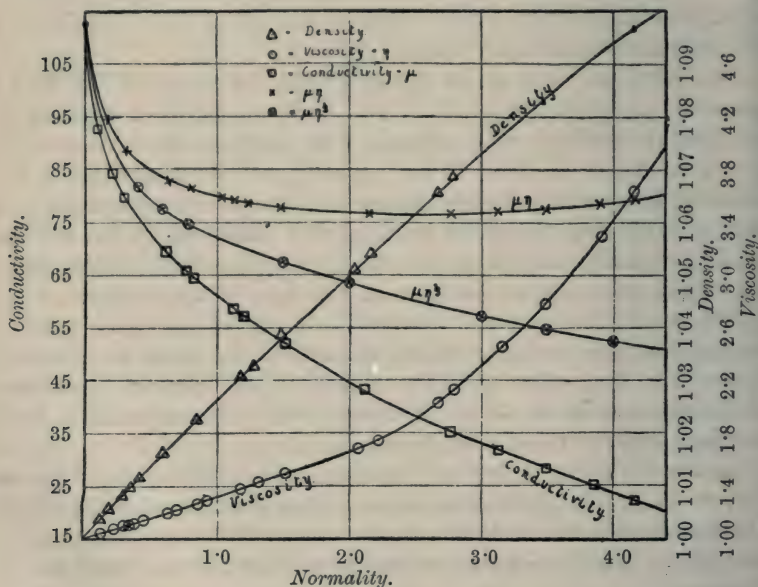
The conductivities were measured in a cell of the usual pattern, having the two electrodes widely separated. In order to eliminate hydrolysis, the water used for making the solutions contained $N/20$ -aniline. Three series of determinations were made, a fresh original solution being used for each.

In the following table these three series are distinguished by the letters *A*, *B*, *C*. The second column gives the normality, the third the density, the fourth the molecular conductivity, and the fifth the viscosity. The density and viscosity are referred to water at 25° as unity.

Series.	Normality.	Density.	Molecular conductivity	Viscosity.	$\mu\eta$.	$\mu\eta^3$.
			= μ .	= η .		
C.	4.1473	1.0970	21.69	3.648	79.14	51.40
C.	3.9182	[1.0921]	23.67	3.297	78.05	52.46
C.	3.4792	1.0827	27.74	2.784	77.22	54.90
C.	3.1149	[1.0752]	31.83	2.437	77.56	57.64
C.	2.7593	1.0685	35.65	2.156	76.86	59.50
B.	2.6608	1.0656	—	2.055	—	—
C.	2.1492	[1.0541]	42.61	—	—	—
B.	2.0470	1.0521	—	1.740	—	—
B.	1.4798	1.0383	52.26	1.498	78.28	68.42
A.	1.1807	1.0308	57.83	1.388	80.24	71.96
B.	1.1083	1.0297	58.59	1.363	79.87	72.02
A.	0.8447	1.0228	—	1.269	—	—
B.	0.8097	[1.0226]	64.90	1.261	81.81	75.63
A.	0.6222	1.0168	69.17	1.193	82.44	77.81
B.	0.6025	[1.0172]	69.70	1.195	83.29	78.49
A.	0.47573	1.0132	72.79	1.149	83.60	79.85
A.	0.36362	1.0107	—	1.118	—	—
A.	0.29308	1.0088	79.80	1.096	87.48	84.83
A.	0.19942	1.0065	84.00	1.070	89.87	87.87
A.	0.10536	1.0037	89.42	1.043	93.78	92.48

The values in brackets were obtained by interpolation.

The results are shown in the accompanying figure, in which the values of the products $\mu\eta$ and $\mu\eta^3$ are obtained from a series of points interpolated on the conductivity and viscosity curves.



It will be seen that the values of $\mu\eta$ attain a minimum at about $V=0.5$, and then on a further increase of concentration remain

nearly constant, with a slight tendency to rise. We can scarcely suppose that the further increase of concentration causes no diminution of dissociation; the true "intrinsic conductivity" must continually decrease with increasing strength, and hence the correction for viscosity in the expression $\mu\eta$ must be too great. If, however, we multiply by the two-thirds power of the viscosity, we get a regularly descending curve. A few values of α , the degree of ionisation, calculated on this latter assumption, are given below.

Normality.	$100 \alpha = \frac{100 \mu\eta^{\frac{2}{3}}}{\mu_{\infty}}$
0.1	82.35
0.5	70.82
1.0	65.21
2.0	56.56
3.0	51.78
4.0	46.34

It does not seem possible at present to establish any theoretical relation between ionic velocity and viscosity. It is a priori probable that some fractional power of the viscosity should be employed, since the viscosity due to the actual ion that is drifting under the potential gradient (which is part of the viscosity as measured in a viscometer) can hardly interfere with the motion of that ion. It is, however, quite possible that the proper index of η is itself a function of η , which approaches unity when η is small, but falls when it is large. Certainly our results indicate that when η is 2 or more, the index $\frac{2}{3}$ is more correct than 1; and this is in agreement with the work of Green (*Trans.*, 1908, **93**, 2023), who found the expression $\mu\eta^{0.7}$ to agree best with experiment for variations of η in the ratio 1:25.

It is to be remembered that at the point where $\mu\eta$ reaches a minimum, the percentage of salt is high (about 26 per cent.). At still higher concentrations a variety of disturbing factors may come in, which might possibly cause an abnormal increase in conductivity, especially the formation of complex ions, and the diminished hydration of the ions, owing to the fall in the concentration of the water. The diminution of hydration, if it occurs at all, must lead to an increase in ionic velocity, and therefore in conductivity; the formation of complex ions will only do so if these ions have a greater velocity than the simple ions, which we should scarcely expect. At any rate, a correction of the conductivity for the viscosity alone, whatever function of the latter may be used, can at best be only an approximation to the truth.

Bousfield (*Phil. Trans.*, 1906, **206**, A, 103) considers that the velocity is inversely proportional to the whole power of the viscosity, and to the radius of the ionic envelope, which latter he

derives on certain assumptions from the solution volume. We have calculated the dissociation constant of aniline hydrochloride on his hypothesis from our results, and find that it rises from 796 in the most dilute solution to 928 in the strongest. It therefore seems unnecessary to give the results of the calculation in full. The values obtained for α on this hypothesis are of the same order as those calculated by Bousfield for other strong electrolytes, such as sodium and potassium hydroxides.

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CXX.—*The Solubility of Aniline in Aqueous Solutions of its Hydrochloride.*

By NEVIL VINCENT SIDGWICK, PERCIVAL PICKFORD, and
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It has long been known that aniline is more soluble in aqueous solutions of its hydrochloride than in pure water; but, except for a few observations of Lidoff (*J. Russ. Phys. Chem. Soc.*, 1883, **15**, 424) on the solubility at 18°, the phenomenon does not seem to have been examined in detail.

We have measured the solubility of aniline in water and in solutions of its hydrochloride of varying strengths, at all temperatures up to complete miscibility. The method adopted was the synthetical: mixtures of aniline, water, and aniline hydrochloride (or hydrochloric acid) in known proportions were heated until they became homogeneous, and then cooled slowly, the temperature of separation being noted. Since the first portions of the new phase which separate are very small in quantity, the composition of the major phase at this temperature may be taken to be that of the whole system. On the curves so obtained, points were interpolated for a regular series of temperatures, and from these points isothermals were drawn, giving the change in the mutual solubility of the two liquids with a change in the concentration of the salt. These curves, however, although they give the complete composition of the saturated liquid, that is, of that liquid with which another liquid phase is in equilibrium, do not tell us anything about the composition of this other phase, except that it lies somewhere on the other branch of the same isothermal. We have therefore determined for one temperature (25°) the partition of the hydrochloride between

the two liquid layers. The combination of these two methods gives a complete knowledge of the conjugate solutions at this temperature. From the isothermal for 25° obtained by the first method, we know the composition of any solution in contact with another liquid phase, if its percentage of salt is given; from the partition-coefficient we know the percentage of salt, and therefore the complete composition of the other phase in equilibrium with it.

Solubility Determinations.

The aniline and its salt were purified as described in the preceding paper. Conductivity water was used throughout.

The solubility determinations were carried out in two ways. At lower temperatures steamed-out Jena flasks were used, with the necks constricted to prevent the condensation of drops of liquid. A known weight of aniline was placed in the flask, and a known weight of hydrochloric acid of the required strength added. The flask was heated in a large beaker of water, and the thermometer (graduated in fifths of a degree, and compared with a standard) was placed in the flask itself. The mixture was heated until it became homogeneous, and then allowed to cool slowly with constant shaking. The critical turbidity, which precedes by a few degrees the actual separation, was always noticed. The point of separation was taken as that at which a small gas flame, seen through the liquid, disappeared. The determination was always repeated several times, and the readings seldom differed by more than 0.2° . When the temperature had been observed, a further quantity of acid (or of aniline) was added, and another reading taken. In this way a series of descending temperatures can be obtained. For higher temperatures the liquids were weighed out into bulbs of Jena-glass, previously steamed, which were then sealed. They were heated in the same way, but in a glycerol bath. In this case the thermometer was, of course, in the bath, but the bulbs being small (about 2 c.c.), and rapidly shaken in the liquid, the error thus produced is not large. The determinations at the highest temperatures (from 150° upwards) are less accurate; they must be made fairly quickly, as the liquid soon begins to decompose and blacken, which renders the results worthless. Hence a repetition with the same tube is often impossible.

In the actual experiments, a series of acids of different strengths (from $N/8$ to $4.5N$) were made. The results are given in table I. They are arranged in the order of increasing amounts of aniline, and hence the temperature first rises and then falls. A , W , S represent the percentages (grams per 100 grams of solution) of free aniline, water, and salt respectively. Since $A + W + S = 100$, it is

unnecessary in any case to give all three, and so on the water side of the curve (composition of the aqueous layer) *W* has been omitted, and on the aniline side, *A*.

TABLE I.

(a) Water.

Temp.	<i>A</i> .	Temp.	<i>A</i> .	Temp.	<i>W</i> .
13·8	3·611	66·0	4·847	160·8	32·88
17·6	3·640	68·6	4·984	154·4	26·60
22·7	3·663	72·3	5·166	153·7	26·14
27·0	3·685	77·1	5·481	150·4	24·12
30·6	3·752	79·7	5·640	127·2	16·58
32·6	3·830	81·6	5·754	97·4	10·43
34·7	3·879	86·6	6·120	74·9	8·088
39·8	3·956	89·9	6·436	66·6	7·47
50·1	4·187	93·4	6·690	59·3	6·94
52·0	4·300	108·8	7·960	51·1	6·49
54·0	4·347	125·3	10·08	43·2	6·078
58·7	4·552	145·1	15·43	35·6	5·720
61·4	4·652	167·0	30·18	27·8	5·406
62·8	4·709	165·0	63·60	20·0	5·123

Critical solution temperature for aniline and water, 168°.

(b) Hydrochloric acid, 0·1245*N*.

Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
27·3	3·913	1·527	167·0	48·47	0·7827
41·6	4·213	1·522	82·1	8·799	0·1412
44·1	4·244	1·521	74·1	8·071	0·1296
52·3	4·551	1·517	66·4	7·455	0·1197
61·8	4·935	1·510	58·3	6·926	0·1112
69·5	5·315	1·505	50·1	6·468	0·1038
70·6	5·373	1·504	42·4	6·066	0·0974
79·2	5·879	1·497	34·6	5·712	0·09169
160·7	24·13	1·206	27·1	5·396	0·08662
			19·1	5·113	0·08208

(c) Hydrochloric acid, 0·2498*N*.

Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
25·8	4·075	3·015	83·3	8·773	0·2850
41·8	4·451	3·009	74·4	8·058	0·2615
54·3	4·870	3·008	66·1	7·433	0·2415
56·1	4·931	2·989	57·3	6·906	0·2243
64·8	5·345	2·995	50·0	6·448	0·2095
73·6	5·888	2·952	41·8	6·048	0·1965
80·1	6·259	2·941	34·1	5·694	0·1850
82·7	6·511	2·939	26·1	5·380	0·1748
156·8	23·70	2·401	17·8	5·098	0·1656
164·3	43·47	1·777			

(d) Acid 0.4980*N*.

Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
17.2	4.195	5.835	151.3	23.29	1.515
31.5	4.574	5.826	138.0	18.78	1.222
44.5	4.920	5.800	79.5	8.960	0.5830
50.9	5.267	5.793	71.0	8.208	0.5340
61.9	5.777	5.745	62.0	7.572	0.4926
66.4	6.071	5.724	53.8	7.027	0.4572
79.3	7.019	5.661	45.9	6.556	0.4265
155.2	60.75	2.390	38.5	6.144	0.3998
			30.5	5.781	0.3761
			21.9	5.456	0.3550

(e) Acid 1.038 and 1.035*N*.

Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
20.2	5.162	11.43	144.0	45.65	4.540
36.1	5.884	11.29	143.4	34.12	4.680
40.2	6.208	11.29	67.5	8.789	1.204
41.0	6.264	11.30	59.1	8.058	1.104
56.4	7.414	11.16	51.3	7.448	1.021
71.5	8.822	10.99	43.1	6.922	0.9485
86.3	11.07	10.72	34.4	6.463	0.8856
89.9	11.55	10.65	26.0	6.067	0.8313
126.8	20.43	9.59			

(f) Acid 1.542*N*.

Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
25.8	7.099	15.835	42.3	7.215	1.483
31.3	7.733	15.73	32.3	6.613	1.359
36.9	8.386	15.62	21.8	6.102	1.254
50.1	10.143	15.32			

(g) Acid 2.045*N*.

Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
20.9	11.78	19.02	108.0	27.95	7.68
43.8	17.92	17.71	111.5	24.72	6.80
49.7	19.59	17.35	102.2	18.95	5.21
64.3	24.08	16.38	84.3	12.27	3.370
72.2	27.19	15.70	51.5	8.778	2.415
77.5	29.78	15.16	42.5	8.055	2.216
92.5	40.87	12.75	33.4	7.441	2.047
104.1	46.00	11.65	24.4	6.916	1.903

(h) Acid 3.030*N*.

Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
3.2	20.98	23.20	72.4	24.67	10.25
11.6	25.48	21.88	72.7	23.29	9.67
39.7	39.00	17.90	71.8	23.89	9.92
42.5	39.14	17.86	72.6	21.99	9.14
49.1	43.08	16.71	71.5	20.55	8.54
51.9	45.46	16.01	69.4	18.65	7.74
55.3	47.37	15.46	68.1	15.25	6.33
61.5	52.21	14.03	68.0	14.77	6.14
63.9	54.25	13.43	54.7	13.02	5.42
67.1	57.66	12.43	46.3	11.29	4.69
69.8	60.44	11.61	36.4	10.02	4.16
71.8	62.89	10.89	28.0	8.732	3.629
70.9	63.97	10.58	18.7	8.012	3.333

(i) Acid 4.00*N*.

Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
20.3	45.90	19.40	39.3	15.04	8.408
27.9	51.87	17.26	30.9	12.11	6.768
35.6	58.79	14.78	9.4	8.915	4.984
41.2	66.89	11.87			

(j) Acid 4.50*N*.

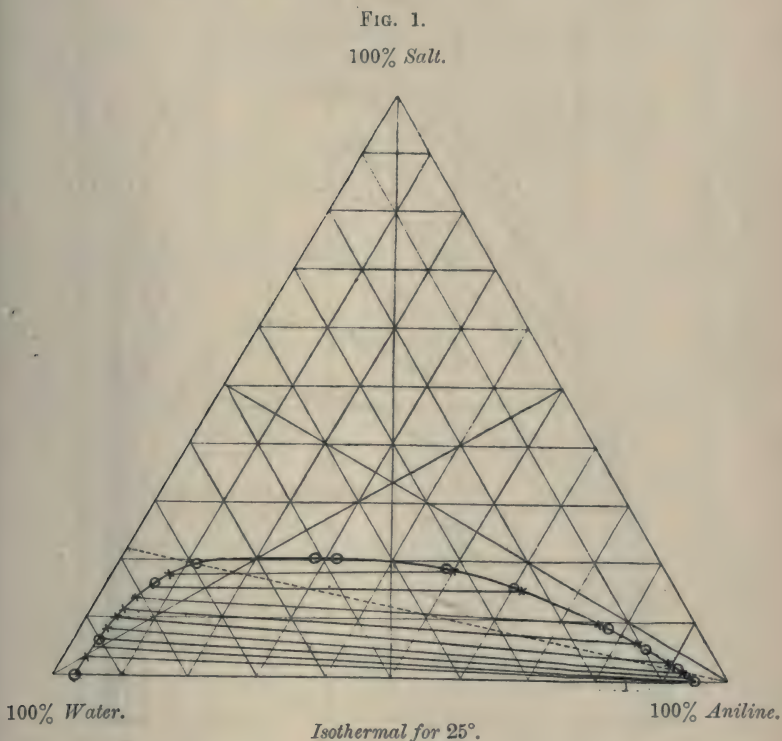
Temp.	<i>A</i> .	<i>S</i> .	Temp.	<i>W</i> .	<i>S</i> .
23.9	58.64	16.06	29.5	17.96	11.40
26.2	61.38	15.00	28.3	15.83	10.05
28.1	64.28	13.87	26.6	14.64	9.30
29.2	67.37	12.67	24.0	13.55	8.60

Table II gives the isothermals obtained by interpolation from the above results, expressed in the same terms.

TABLE II.

<i>a</i> . Isothermal for 15°.				<i>b</i> . Isothermal for 25°.			
<i>A</i> .	<i>S</i> .	<i>W</i> .	<i>S</i> .	<i>A</i> .	<i>S</i> .	<i>W</i> .	<i>S</i> .
3.615	0.000	7.276	3.025	3.681	0.000	14.00	8.884
3.791	1.529	7.231	1.989	3.882	1.528	10.84	6.062
4.144	5.826	5.816	1.195	4.020	3.020	8.371	3.479
4.940	11.44	5.717	0.7834	4.378	5.842	6.949	1.912
5.995	16.03	5.230	0.3403	5.380	11.40	6.238	1.282
10.44	19.35	5.006	0.1627	7.023	15.83	6.043	0.8278
26.80	21.49	4.960	0.08011	11.86	19.02	5.568	0.3623
		4.942	0.00000	31.35	20.15	5.327	0.1731
				49.25	18.20	5.311	0.08899
				59.95	15.55	5.299	0.00000
<i>c</i> . Isothermal for 40°.				<i>d</i> . Isothermal for 60°.			
<i>A</i> .	<i>S</i> .	<i>W</i> .	<i>S</i> .	<i>A</i> .	<i>S</i> .	<i>W</i> .	<i>S</i> .
3.941	0.000	15.65	8.752	4.58	0.000	14.27	5.93
4.187	1.523	10.21	4.243	4.87	1.512	9.569	2.632
4.371	3.009	7.874	2.166	5.13	2.984	8.109	1.112
4.823	5.815	7.069	1.452	5.67	5.762	7.492	0.4876
6.210	11.30	7.058	0.9669	7.69	11.14	7.051	0.2284
8.779	15.55	6.225	0.4052	11.63	15.25	7.047	0.1138
16.88	17.94	5.938	0.1929	22.80	16.66	7.030	0.0000
38.69	18.00	5.940	0.09596	51.10	14.36		
64.20	12.84	5.930	0.00000				
<i>e</i> . Isothermal for 80°.				<i>f</i> . Isothermal for 100°.			
<i>A</i> .	<i>S</i> .	<i>W</i> .	<i>S</i> .	<i>A</i> .	<i>S</i> .	<i>W</i> .	<i>S</i> .
5.66	0.000	12.31	3.387	7.10	0.000	41.57	11.45
5.95	1.495	9.848	1.350	7.68	1.467	18.16	4.995
6.26	2.950	8.998	0.5857	8.10	2.891	12.76	1.748
7.11	5.678	8.524	0.2769	9.60	5.522	11.37	0.1836
9.95	10.85	8.512	0.1387	13.60	10.41	11.90	0.0000
31.18	14.85	8.500	0.0000				
<i>g</i> . Isothermal for 120°.				<i>h</i> . Isothermal for 140°.			
<i>A</i> .	<i>S</i> .	<i>W</i> .	<i>S</i> .	<i>A</i> .	<i>S</i> .	<i>W</i> .	<i>S</i> .
9.30	0.000	17.94	2.459	13.75	0.000	29.52	4.043
21.21	9.497	14.45	0.000	38.75	7.384	21.09	0.000

For the graphic representation of a three-component system such as this, the best method in theory is to use a triangular diagram, the proportion of each component being measured along the perpendicular from the middle of one side to the opposite angle. The isothermal for 25° is plotted in this way in Fig. 1. The lines across the curve are "tie-lines," joining points representing conjugate solutions, that is, two layers in equilibrium. The method by which they are obtained is described in the next section. The experimental curves, in which the ratio of water to salt remains constant, would



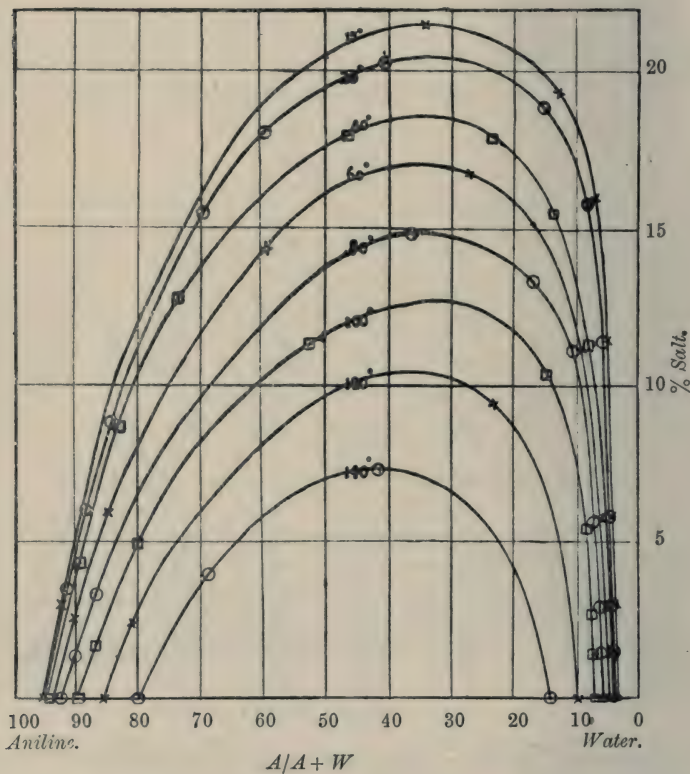
be represented on this diagram by straight lines drawn from the apex to the side water-salt, and dividing this side in that ratio; one of these, corresponding to the experiment with twice normal salt (table I, *g*), is shown by the dotted line in the figure. The drawback to this method is that, owing to the small percentage of salt necessary to produce complete miscibility at even the lowest temperatures investigated, the curves occupy only a small part of the triangle, and so are inconveniently crowded; thus all the isothermals for temperatures above 25° would lie within the one

given in the diagram. It is more convenient, although less logical, to use a rectangular diagram, in which one axis represents the proportion of salt, and the other the ratio of free aniline to aniline plus water ($A/A + W$). This is given in Fig. 2.

Measurement of the Partition-coefficient.

In order to determine the partition of the salt between the two liquid phases, and its variation with the concentration, the mixture

FIG. 2.

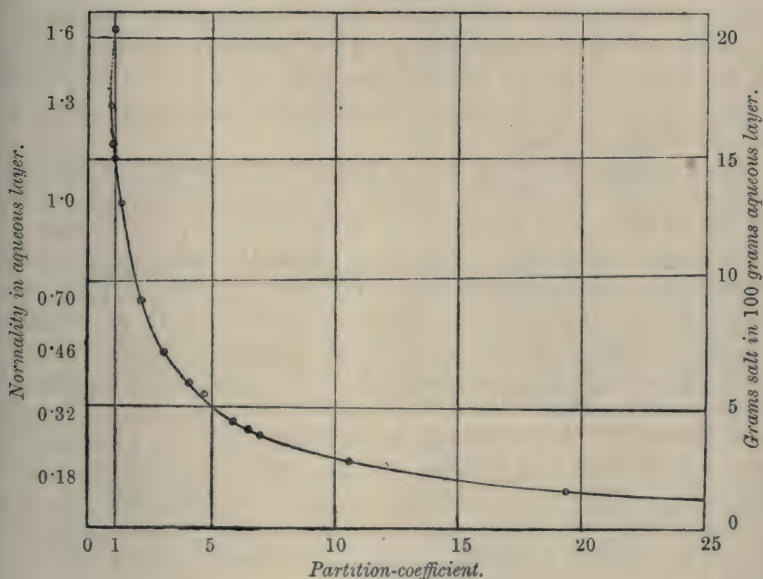


of aniline, salt, and water was stirred in a thermostat at 25°, and the two layers were analysed. The liquid was rapidly stirred with a glass stirrer, passing through a mercury trap to prevent evaporation for about an hour, and was allowed to settle. A quantity of each layer was then drawn off in a weight-pipette, which had previously been warmed to the temperature of the bath. The chlorine was estimated gravimetrically as silver chloride with a

Gooch crucible. The analyses were made in duplicate, and in many cases a second series of samples were removed and analysed after a further stirring for one or two hours, but no change in composition was observed.

The results are given in the following table; C_{aq} is the weight-normality of the salt in the aqueous layer, C_{an} that in the aniline layer, and p is the ratio of these two, that is, the partition-coefficient.

FIG. 3.



The values of p are plotted against the normality of the aqueous layer in Fig. 3.

TABLE III.

Partition-coefficient.

C_{aq}	C_{an}	p	C_{aq}	C_{an}	p
0.1110	0.005989	19.30	0.5514	0.1816	3.038
0.2039	0.01939	10.52	0.7126	0.3371	2.073
0.2892	0.04190	6.889	1.0247	0.8558	1.234
0.3117	0.04886	6.388	1.1622	1.1299	1.029
0.3361	0.05758	5.838	1.1832	1.1876	0.9980
0.4240	0.09151	4.631	1.3320	1.466	0.9087
0.4594	0.1134	4.044			

It will be seen that the partition, which in dilute solution is greatly in favour of the water, becomes unity at a little over normal, and in stronger solutions is in favour of the aniline. It is obvious that at the point where the two layers become identical, that is,

where there is the maximum concentration of salt compatible with the existence of two layers, the salt must be equally distributed between them. The partition-coefficient must therefore diminish again with increasing concentration of salt, and finally attain the value 1 where the amount of salt is at the maximum of the isothermal. This is indicated on the diagram by the dotted line.

If we take a point on the isothermal for 25° (Fig. 1), say, on the water side, we know the amount of salt in this solution; from the partition curve we can determine the amount of salt in the other layer; and the point on the other side of the isothermal corresponding with this amount of salt gives us the complete composition of the aniline layer in equilibrium with the first solution. The cross lines on Fig. 1 connect a series of conjugate solutions calculated in this way.

The solubility at 25° of aniline hydrochloride in pure water and in pure aniline was also determined, and was found to be (in grams of salt to 100 grams of solution), in water 52.1 ($=4.02N$), and in aniline 8.89 ($=0.686N$). From these data the solubilities can be calculated by means of the law of mixtures for various conjugate solutions, but the partition ratios so deduced bear no obvious relation to those observed. Thus at extreme dilutions of salt, when the solvents are practically pure, the ratio should be that of the solubilities, that is, $52.1 \div 8.89 = 5.85$. But, in fact, it is over 20. This might be explained by assuming that the partition of the undissociated salt between the two layers is constant, which would also account qualitatively for the striking fall in the partition-coefficient with increasing concentration. The experiments described in the preceding paper were begun with a view of throwing light on this question. They are, however, applicable only when the concentration of salt is very small, and the two solvents are therefore nearly pure. The determination of the degree of ionisation in various mixtures of aniline and water is practically impossible. As is pointed out in the preceding paper, we do not know for certain how to correct for changes in the viscosity, which in mixtures rich in aniline attains a value of more than 10. Still less do we know how far the aniline affects the ionic velocity through the solvation. A direct measurement of this velocity by extrapolation from dilute solutions is impossible, since a mixture of water and aniline containing more than a small proportion of the weaker constituent cannot be obtained at all unless a fair amount of salt is present.

We have, however, made a few measurements, which give rather curious results. The method adopted was to keep the concentration of salt constant, while the ratio of aniline to water was varied. In

order to get a continuous series of solutions, the amount of salt taken was 22 grams per 100 grams of solution (normality = 1.72). Two solutions of this strength, in aniline and water, were made up, and were mixed in various proportions. The solution in pure aniline crystallised out above 25°, but the addition of 1 per cent. of the aqueous solution sufficed to dissolve the salt. The solutions were made up by weight. The results are given in the following table. The first column gives the ratio of aniline to aniline + water, the second the density, the third the viscosity, and the fourth the molecular conductivity.

$\frac{100 A}{A+W}$	Δ	η	μ obs.	μ calc.	$\mu\eta$	$\mu\eta^3$
95.24	1.0633	12.85	1.822	2.31	23.41	9.693
82.43	1.0612	7.617	7.160	8.53	54.54	27.72
70.64	1.0582	5.967	12.58	14.26	75.03	41.37
59.05	1.0553	5.009	17.89	19.89	89.61	52.32
49.74	1.0518	4.371	22.09	24.41	96.54	59.03
36.81	1.0502	3.571	27.87	30.69	99.58	65.1
00.00	1.0418	1.600	48.57	(48.57)	77.71	65.8

If these results are plotted, it is seen that the conductivity, μ , is practically a straight line, which would cut the aniline axis at zero, or nearly so. This would seem to indicate that the amount of dissociation is simply proportional to the amount of water present. The values of the conductivity calculated on this assumption (μ for aqueous solution $\times \frac{W}{A+W}$) are given in the fifth column.

Such a conclusion, however, leaves out of account the enormous change in viscosity, and the unknown but presumably considerable effect of the change in solvation. It is certainly remarkable, if it is a mere coincidence, that the combination of all these factors (to which, no doubt, others, such as the change in the dielectric constant, should be added) results in an exact proportionality. At any rate, the same relation seems to hold for other concentrations of the salt as well, as the following measurements show; the values in the last column are obtained by multiplying the conductivity of an aqueous solution of the same salt-concentration by the proportion of water in the solvent.

S	$\frac{100 A}{A+W}$	η	μ obs.	μ calc.
19.61	9.85	1.816	45.5	45.7
27.39	23.81	2.900	31.0	31.0
25.43	39.60	3.903	24.6	26.1
24.36	52.09	4.756	19.0	21.2

Although we have not succeeded in deducing any quantitative relations, the qualitative relations are fairly clear. If we add to a system of two liquid phases a third component, two opposite effects

may be produced. If the third component dissolves only in one layer, the solubility of each liquid in the other will be diminished; in fact, in this extreme case the diminution can be calculated from the diminution of vapour pressure, and this has actually been proposed as a means of determining molecular weights. On the other hand, if the third component divides itself more or less equally between the two phases, the solubility of each of the two original liquids in one another will increase, as occurs, for example, when alcohol is added to nitrobenzene and water. Between these two extremes lie an infinite number of intermediate stages, in which the third substance dissolves in both layers, but in unequal degrees. Hence the addition may either increase or diminish the mutual solubility of the two liquids, according as the partition is equal or unequal. The peculiarity of the system we have examined is that this partition varies greatly with the concentration of the salt. In dilute solutions, owing, presumably, to its high degree of ionisation, the salt is very unequally divided between the two layers, and, in consequence, the increase in the mutual solubility is almost imperceptible. In stronger solutions, the distribution is much more equal, and so the increase in solubility is very little affected by the first additions of salt, and much more by subsequent additions, when p is approaching unity. It is also easy to see why the curves, at low concentrations, slope much more on the aniline than on the water side. The increase of solubility depends on the modification, not only of one, but of both layers. Owing to the high value of the partition-coefficient, the addition of, say, 1 per cent. of salt to the aqueous layer implies a much smaller increase of salt in the aniline layer, and, conversely, the addition of 1 per cent. of salt to the aniline layer involves a much greater modification of the conjugate aqueous layer.

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CXXI.—*The Solubility of Electrolytes in Aqueous Solutions. Part I. Solubility of Salts in the Corresponding Acids.*

By JAMES IRVINE ORME MASSON (1851 Exhibition Scholar
of the University of Melbourne).

THE precipitation of sparingly soluble salts from aqueous solution by addition of an electrolyte with a common ion has been studied by Nernst, Noyes, and others, and the results have been shown to

be in harmony with the simplest ionic conceptions. It is recognised, however, that when concentrated solutions of strong electrolytes are dealt with, these conceptions are insufficient for quantitative explanation of the results. The chief work on this class of solutions is by Engel (*Compt. rend.*, 1886, **102**, 619; 1887, **104**, 433; *Ann. Chim. Phys.*, 1888, [vi], **13**, 132), who has determined the solubilities at 0° of numerous chlorides in hydrochloric acid of varying concentration, and of several nitrates in nitric acid. His results led him to an empirical rule, which holds for moderate strengths of acid, namely, that the introduction of acid into the saturated salt solution precipitates a chemically equivalent quantity of salt. This rule is put forward as an approximation; and it fails completely in certain cases omitted by Engel, as the sequel shows. Armstrong and others have made similar determinations with chlorides of the alkali metals (*Proc. Roy. Soc.*, 1907, *A*, **79**, 564; 1910, *A*, **84**, 123). The results are interpreted on the supposition that the reduction of solubility of the salt is caused by appropriation of solvent molecules by the acid introduced, and figures are given for the "apparent molecular hydration" of the precipitant. No quantitative statement is made to show how the hydration values obtained are governed by the concentrations.

The object of the present work was to extend that of Engel, and to elucidate, if possible, the conditions governing the solubilities of salts in aqueous solutions of their acids, for cases and for concentrations to which Engel's rule does not apply.

The solubilities which have been studied are those of sodium chloride and of barium chloride in hydrochloric acid, and those of silver nitrate and of barium nitrate in nitric acid. The measurements, which were made at 30°, were supplemented by determinations of specific gravity. The first two cases were studied by Engel at 0°; the others do not seem to have hitherto been investigated.

EXPERIMENTAL.

The solutions were made up in small flasks provided with well-ground stoppers. Concentrated salt solution, acid, and water were separately heated to about 45° in a water-bath, and mixed in suitable proportions in the heated flasks, which were left for half an hour at 45°. These were then quickly shaken, and transferred to a thermostat at 30°, where they remained, with only the stoppers projecting, for times ranging from two to six days, during which period they were occasionally shaken quickly but effectively. The saturated solutions containing no acid were made up in a similar manner, except that a higher initial temperature was used.

That the precautions taken against supersaturation were sufficient

is apparent from the uniformity of the results with one another (as evinced by the smoothness of the curves obtained), and with such measurements by other workers as are available. It may be pointed out that Andrae has proved that the same solubility limit is reached by the method of cooling as by that of agitating solid and solvent together at the required temperature.

The temperature of the thermostat was kept at $30.00^{\circ} \pm 0.03$ by a toluene gas-regulator, and was measured with a standard thermometer. During introduction of the solutions and density determinations, a stirrer was set in motion.

Withdrawal of the solutions for examination was effected either by sucking the liquid through a warmed siphon provided with a filter-plug, into a receiver contained in the thermostat, or by using a warmed pipette with a detachable filter-cap containing glass wool. Both methods admitted of rapid sampling, without causing precipitation to occur through cooling of the liquid. The filtered solution was transferred by means of a pipette into a density-bottle suspended in the thermostat, and the capillary stopper inserted; after five minutes the bottle was removed, and, when cold, weighed. The bottles were each provided with a glass cap to prevent evaporation during cooling and weighing. They were standardised with pure water at 30° ; and duplicate determinations showed that the specific gravity results may be taken as correct to the fourth decimal place.

Analysis.—The density-bottle, containing solution and deposited crystals, was carefully washed out, and the liquid diluted to a known volume. As a rule, this solution was of strength convenient for the determination of both ingredients; if one of these, however, was present in small quantity only, it was determined in a separate sample of the original solution, which was taken with a warmed standard pipette and diluted to a convenient bulk.

All analyses were made in duplicate, and the results tabulated are the means of closely concordant observations.

Acidity was measured by titrating an aliquot part of the sample with $N/10$ -potassium hydroxide, using methyl-orange as indicator. With mixtures of silver nitrate and nitric acid, it was necessary first to remove the silver by shaking with slight excess of pure neutral sodium chloride solution, the filtered liquid being then titrated with potassium hydroxide.

Salt-content:—Chlorides were determined by difference, the acidity value of the hydrochloric acid present being subtracted from the total chlorine concentration; this was measured by adding excess of $N/10$ -silver nitrate in known quantity, and titrating the residual silver in the filtered liquid and washings with $N/10$ -ammonium thiocyanate. The solubility of sodium chloride in

pure water was also determined by evaporating in a platinum vessel measured volumes of the saturated solution, fusing and weighing the salt. The result was in complete agreement with that obtained volumetrically, and also with the determinations of Andreae (*J. pr. Chem.*, 1884, [ii], **29**, 456).

Barium nitrate was determined either (1) by precipitating with ammonia and ammonium carbonate; after filtration and washing, the precipitate was dissolved in a known quantity of $N/5$ - or $N/10$ -acid, the residual acid being then titrated with $N/10$ -potassium hydroxide; or (2) gravimetrically as sulphate. The two methods gave practically identical results.

Silver nitrate was determined by direct titration with $N/10$ -ammonium thiocyanate.

In all cases, the crystals deposited in the original solutions were examined, after being dried with absorbent pads, and were then found to contain only small traces of free acid. Barium chloride, even when totally displaced from solution by hydrochloric acid, was precipitated as the pure dihydrate, as analysis showed.

The standard solutions were compared ultimately with an approximately normal solution of pure hydrochloric acid, the strength of which was exactly determined with Iceland spar (Orme Masson, *Chem. News*, 1900, **81**, 73). This was used to standardise the potassium hydroxide and the silver nitrate; the latter was in turn used for the thiocyanate. In each case the method used was that to be applied to the analyses. Other methods were resorted to as checks; and the strengths of the standard solutions were trustworthy to 1 in 1000.

The salts and acids employed were of the purest commercial quality, and were dissolved in freshly distilled water.

Results.

The symbols used in the tables are as follows:

S = specific gravity at 30.0° (water = 0.9957);

a = gram-molecules of acid per litre of solution measured at 30° ;

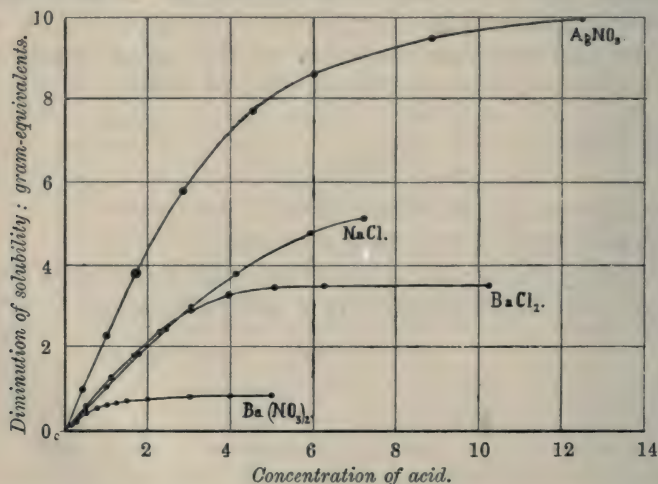
b = gram-molecules of salt per litre of solution measured at 30° .

TABLE I.

HCl - NaCl.			HCl - BaCl ₂ .		
<i>S.</i>	<i>a.</i>	<i>b.</i>	<i>S.</i>	<i>a.</i>	<i>b.</i>
1·2018	0·0000	5·400	1·3056	0·0000	1·745
1·1906	0·4575	4·932	1·2651	0·4709	1·468
1·1801	0·969	4·386	1·2147	1·107	1·122
1·1633	1·786	3·589	1·1789	1·622	0·861
1·1512	2·412	2·978	1·1419	2·234	0·592
1·1427	3·052	2·463	1·1068	3·041	0·307
1·1289	4·152	1·628	1·0880	3·953	0·124
1·1188	5·950	0·630	1·0895	5·059	0·020
1·1258	7·205	0·268	1·1024	6·234	0·00
			1·1609	10·25	0·00

HNO ₃ - Ba(NO ₃) ₂ .			HNO ₃ - AgNO ₃ .		
<i>S.</i>	<i>a.</i>	<i>b.</i>	<i>S.</i>	<i>a.</i>	<i>b.</i>
1·0891	0·0000	0·4270	2·3921	0·0000	10·31
1·0811	0·1318	0·3682	2·2754	0·4042	9·36
—	0·2496	0·3268	2·1243	0·962	8·08
1·0663	0·4995	0·2410	1·9402	1·698	6·54
1·0619	0·7494	0·1785	1·7052	2·834	4·526
1·0609	1·000	0·1353	1·4980	4·497	2·590
1·0633	1·247	0·1056	1·4195	5·992	1·698
1·0668	1·493	0·0847	1·3818	8·84	0·843
1·0783	1·998	0·0598	1·3976	12·53	0·347
1·1050	2·993	0·0334			
1·1341	3·986	0·0218			
1·1341	3·994	0·0223			
1·1645	5·012	0·0147			

In the following diagram are plotted the curves showing the relation of the diminution of solubility to the acid content; for



convenience of scale, concentrations are here expressed in gram-equivalents per litre.

Discussion of Results.

(a) *Solubility*.—It is obvious on inspection of the figure that the empirical rule of Engel does not apply to the cases of the two nitrates here studied. It is, however, correct to a limited extent for the two chlorides; and a modification of the rule may therefore be sought, which may cover all the results. It has been found that the expression:

$$-\frac{da}{db} = k_0 + k\frac{a}{b},$$

in which k_0 and k are constants in any given case, represents with considerable accuracy practically the entire course of all four curves, and also holds when applied to the results obtained at 0° by Engel for numerous salt-acid solutions. Engel's rule is the special case in which the initial slope $k_0=1$, and $k=0$. The integrated form of the equation is:

$$\frac{a}{b} = \frac{k_0}{k+1} \left\{ \left(\frac{B}{b} \right)^{k+1} - 1 \right\},$$

in which B is the value of b when $a=0$. The following table contains the calculated and found concentrations of acid corresponding with the experimental solubilities of the salts; the figures for the constants, which are ascertained by trial, are also tabulated.

TABLE II.

Values of a.

HCl - NaCl.		HCl - BaCl ₂ .		HNO ₃ - Ba(NO ₃) ₂ .		HNO ₃ - AgNO ₃ .	
Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.
0.45	0.46	0.48	0.47	0.13	0.13	0.39	0.40
0.98	0.97	1.11	1.11	0.23	0.25	0.94	0.96
1.79	1.79	1.62	1.62	0.49	0.50	1.68	1.70
2.44	2.41	2.22	2.23	0.75	0.75	2.87	2.83
3.03	3.05	3.04	3.04	1.01	1.00	4.60	4.50
4.09	4.15	3.95	3.95	1.26	1.25	5.98	5.99
5.91	5.95	5.81	5.06	1.51	1.49	8.66	8.84
7.26	7.20			1.97	2.00	13.3	12.5
				3.00	2.99		
				4.04	3.99		
				3.95	3.99		
				5.31	5.01		
k_0	0.95	1.71		2.12		0.40	
k	0.18	0.19		0.68		0.46	

Engel's results at 0° have been tested, and found to agree with the formula. In the case of sodium chloride, $k_0=0.84$, $k=0.30$; for barium chloride, $k_0=1.79$, $k=0.18$.

(b) *Specific Gravity*.—If it is assumed, in the first instance, that solvent water has the same density as pure water, the equation:

$$1000 (S - 1) = a \left(\frac{M_a}{\delta} - \alpha \right) + v \left(\frac{M_b}{\delta} - \beta \right)$$

follows, in which:

δ = the density of water at the experimental temperature,

M_a and M_b = molecular weights of acid and of salt respectively, and

α and β = the respective volumes in c.c. of one gram-molecule of each.

On applying this equation to the experimental data, the somewhat unexpected result is obtained that the coefficients of a and b prove to be constants, and hence that the molecular volumes of the solutes are independent of their concentrations. It appears, therefore, that in this respect mixed electrolytes differ from single electrolytes, the molecular solution volumes of which vary considerably with concentration. The equation may thus be written:

$$1000(S - 1) = ma + nb \quad . \quad . \quad . \quad (1),$$

m and n being constants.

The validity of the foregoing statements can be judged by the accuracy with which the specific gravities may be calculated, the values of m and n in a given series being found from two experimental points. In the second row of table III, which gives the results in the typical case of sodium chloride, are shown the figures calculated by means of equation (1).

TABLE III.

Values of $S - 1$; HCl—NaCl Series.

Found:	0.2018	0.1906	0.1801	0.1633	0.1512	0.1427	0.1289	0.1188	0.1258
Cal. (1).	0.2017	0.1922	0.1801	0.1636	0.1510	0.1421	0.1289	0.1209	0.1279
Cal. (2).	0.2000	0.1905	0.1791	0.1633	0.1511	0.1424	0.1288	0.1186	0.1237

The derived values for the molecular solution volumes are:

{ HCl	20.2	{ HCl	19.9	{ HNO ₃	30.5	{ HNO ₃	30.5
{ NaCl	21.3	{ BaCl ₂	34.0	{ Ba(NO ₃) ₂	55.2	{ AgNO ₃	27.6.

Engel's data for 0° agree with the formula fairly well. They show that hydrochloric acid has different molecular solution volumes when mixed with different salts.

Whilst equation (1) is a sufficiently accurate expression of the facts for a wide range of concentration, its applicability diminishes at the highest strengths of acid. This is doubtless due to the assumption that the density of water is independent of the presence of substances in solution. If now the molecular solution volume of the solvent water is admitted to differ from that of the pure liquid, the equation which results is:

$$\gamma w + \alpha a + \beta b = 1000 \quad . \quad . \quad . \quad (2),$$

in which w is the concentration, and γ the molecular volume of the water; the other symbols retain their previous meanings. Calculation from three experimental points in a given series show that α , β , and γ are constants; and the values so obtained may be used to deduce figures for w from those of a and b at other concentrations. Table IV gives the result for barium chloride-hydrochloric acid solutions, as a typical example; and it is seen that the agreement with experiment is such as to offer strong evidence of the actual constancy of the molecular solution volumes.

TABLE IV.

Water Concentrations; HCl—BaCl₂ Series.

Calc. ...	51.97	52.00	51.98	51.92	51.76	51.40	50.69	49.58	48.21	43.25
Found ..	51.97	51.99	51.92	51.92	51.73	51.46	50.69	49.74	48.30	43.41
(α=21.7; β=38.8; γ=17.9).										

For reckoning specific gravities, equation (2) may be transformed into $S = K + k_1a + k_2b$, the constants of which can be directly calculated from α , β , and γ . The results for sodium chloride are given in the third row of table III, and it will be seen that they are more closely in harmony with the facts than are those of equation (1).

The molecular solution volumes of water in the four cases, as derived from equation (2), are: Ba(NO₃)₂ series, 18.1; BaCl₂, 17.9; NaCl, 17.7; AgNO₃, 17.3, the order of magnitude being the reverse of that of the solubilities of the salts. The molecular volumes of nitrates in solution are greater than those of chlorides; but any more particular statement would demand more numerous examples than are as yet available.

Summary.

(1) The experimental work consists of determinations at 30° of the solubilities of four simple salts in water containing varying concentrations of the corresponding acids, and includes measurements of the specific gravities of the solutions.

(2) A simple differential equation has been found which expresses well the relation between the concentrations of acid and of salt. The equation is in accord with Engel's solubility data at 0°.

(3) Two formulæ are given whereby the specific gravities of the solutions may be calculated. It appears from these that the molecular volumes of water, acid, and salt remain constant through wide ranges of concentration.

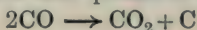
The work described was carried out at the suggestion of Professor Orme Masson.

CXXII.—*The Effect of Temperature and of Pressure on the Equilibrium $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$.*

By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

IN extension of van't Hoff's principle of mobile equilibrium to include all the factors that determine chemical equilibrium in gaseous systems, Le Chatelier's theorem states that any change in the factors of equilibrium from outside is followed by a reverse change within the system.

At constant temperature and pressure the reaction



is accompanied by a decrease in volume. A decrease in pressure should, therefore, increase the proportion of carbon monoxide in the system $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ in equilibrium at constant temperature.

The general formula deduced by Le Chatelier:

$$500 \int L \frac{dT}{T} + (N' - N) \log_e P + \log_e \frac{C_1^{n_1} C_1'^{n'_1} \dots}{C_2^{n_2} C_2'^{n'_2} \dots} = k,$$

which, when P was assumed constant and equal to one atmosphere, we have shown to hold for changes in temperature (Trans., 1910, 97, 2178), contains the expression $(N' - N) \log_e P$, by means of which changes in pressure should be accounted for.

When $P=1$, this expression disappears from the formula, and on introducing the known values for the system under consideration, the equation becomes:

$$\frac{19,500}{T} + \log_e \frac{C_1^2}{C_2} = k.$$

In our previous communication we have given values for k for different temperatures, calculated from this equation, the method of experiment being such as to leave the gases under as nearly as possible atmospheric pressure when equilibrium had been reached.

We are not acquainted with any previous attempts to prove whether the expression $(N' - N) \log_e P$ in Le Chatelier's general equation satisfies experiment in this particular case, and since the matter is one of considerable importance in several allied investigations, we have undertaken its determination.

Since for the system $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$, $N'=2$ and $N=1$, the effect on k of pressure should be measured directly by the natural logarithm of the value of the latter in atmospheres, and the determination of k for different pressures at any one temperature should be sufficient to verify the equation.

Our former values for k at different temperatures showed, however, a tendency towards an increase as the equilibrium temperature was increased. We were therefore desirous of ascertaining whether this is actually the case, or whether the alterations in the value of the constant should be ascribed solely to experimental error. For this purpose we have made a considerable number of determinations of the percentages of carbon dioxide and monoxide remaining in equilibrium over carbon at different temperatures and pressures, reaching the equilibrium from both directions.

Our method of experiment, which is described in detail later, is very similar to that employed by Boudouard (*Ann. Chim. Phys.*, 1901, [vii], **24**, 5), the chief difference being that whereas Boudouard's determinations were all made at constant pressure (atmospheric), ours have been chiefly at constant volume, the pressure produced by the expansion of the gases on raising them to the experimental temperature, and (when starting with an initial concentration of 100 per cent. carbon dioxide) by the formation of two volumes of carbon monoxide for each volume of carbon dioxide changed, enabling us to study the effect of a fairly high pressure on the equilibrium values.

The values obtained for the equilibrium constant at any one temperature for different pressures agree remarkably well, as the following determinations at 1273° Abs. (the temperature at which the majority of our experiments have been made) show:

Experiment No. P 10. Temperature = 1273° Abs.

Pressures, atmospheres.	C_1 .	C_2 .	k .
3.08	0.9723	0.0277	19.98
2.43	0.9776	0.0224	19.96
2.02	0.9837	0.0163	20.11
1.56	0.9856	0.0144	19.98
0.66	0.9935	0.0065	20.14

We are therefore justified in introducing values for $\log_e P$ in the equation:

$$\frac{19,500}{T'} + \log_e P + \log_e \frac{C_1^2}{C_2} = k. \quad . \quad . \quad . \quad (i)$$

to correct for divergencies from 760 mm. pressure in our previous series of determinations.

At the same time we may remark that an error of 10° in either direction in the measurement of temperature alters the value of the constant by a quantity decreasing from 0.16 at 1123° Abs. to 0.09 at 1473° Abs. Errors in analysis of the gases have a greater effect on the constant at high than at low temperatures; that is to

say, the effect of error is greater when the percentage of carbon dioxide present is small. If, for example, 6.25 per cent. of carbon dioxide were remaining in equilibrium at 1123°, instead of the 6.23 per cent. recorded, the numerical value of the constant alters only in the third decimal place; whilst at 1473° a similar error of 0.02 per cent. in the determination of carbon dioxide alters the value of the constant from 20.65 to 20.36.

We give below our previous values for k at different temperatures corrected for pressure, and also the corrections to be applied for an error of 10° in the temperature measurements and of 0.02 per cent. in the determination of carbon dioxide.

Temperature. Abs.	k .	Correction for error of 10° in measurement of temperature.	Correction for error of 0.02 per cent. in estimation of carbon dioxide.
1123	20.00	± 0.16	nil
1173	20.29	0.15	nil
1223	20.23	0.14	± 0.02
1273	20.36	0.12	0.03
1323	20.30	0.11	0.04
1373	20.58	0.10	0.14
1473	20.60	0.09	0.29

It will thus be seen that, if one assumes both errors to lie in the negative direction at the higher, and in the positive direction at the lower temperatures, the apparent increase in the value of the constant at high temperatures loses its significance so long as only a few determinations are relied on; for we cannot pretend to an accuracy of 0.02 per cent. in the estimation of small quantities of carbon dioxide. When, however, as in the present case, a number of closely agreeing values are obtained at each temperature, one is justified in considering either that the experimental error is not so great as surmised, or, what is more probable, that the "personal factor," which exercises its influence particularly on gas analysis, tends to throw the error always in the same direction.

Our results again indicate an increase in the value of the equilibrium constant with increased temperature, as calculated from equation (i). The numbers increase from an average of 19.85 for 1073° Abs. (pressures from 1 to 3 atmospheres) to 20.16 for 1373° Abs. (pressures from 0.5 to 3 atmospheres).

These values, and those for intermediate temperatures given in the table that follows, are lower than those previously given, a result which we must attribute to differences in the experimental method employed. In particular, an unavoidable alteration in the method of measuring the temperatures appears to us most likely to render the results of the two series not strictly comparable. In

the former series a protected thermo-couple was embedded in the carbon, whilst in the present series the thermo-couple had to be placed outside the reaction vessel, and was in immediate contact with the furnace tube. The average temperature of the reacting surface may therefore have been lower than the recorded temperature in the present series, whilst in the former arrangement the carbon near the walls of the porcelain tube was possibly at a higher temperature than that immediately surrounding the thermo-couple.

The mean values at different temperatures of those obtained at all pressures are:

Temperature.	
Abs.	<i>k</i> .
1073	19·85
1173	19·96
1223	20·01
1273	20·04
1322	20·14
1373	20·17

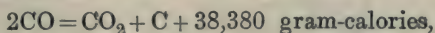
We do not think that the progressive increase in the value of *k*, which appears to be a linear increase over the range of temperature studied, should be ignored. We presume it to be due to the decrease with temperature of the value of *L* (the total heat of the reaction), dependent on the difference of the specific heats of the two systems, for which no allowance is made in Le Chatelier's equation.

Assuming for the moment a linear increase in the value of the constant, which can then be expressed as a function of *T* and has a value $18\cdot777 + 0\cdot001 T$, calculation gives the following quantities of carbon dioxide and carbon monoxide in equilibrium over carbon at atmospheric pressure and at different temperatures:

Temperature.	CO.		CO ₂ .	Value of <i>k</i> used.
	Abs.	<i>C</i> ₁ .	<i>C</i> ₂ .	
1073		0·8615	0·1385	19·85
1123		0·9313	0·0687	19·90
1173		0·9663	0·0337	19·95
1223		0·9833	0·0167	20·00
1273		0·9915	0·0085	20·05
1323		0·9955	0·0045	20·10
1373		0·9975	0·0025	20·15

We will now substitute a corrected value for *L_T* in equation (i), and determine the value of the equilibrium constant on introducing the values for *C*₁ and *C*₂ given in the above table.

Taking the heat of reaction at ordinary temperatures and at constant volume to be



we have for the difference between the molecular heats of factors and products * :

$$\begin{array}{r|l}
 2\text{CO} = 8.94 + 0.0012T & \\
 \text{CO}_2 = & 5.28 + 0.0026T \\
 \text{C} = & 1.64 + 0.0017T \\
 \hline
 (8.94 + 0.0012T) - (6.92 + 0.0043T) & \\
 = 2.02 - 0.0031T &
 \end{array}$$

from which is obtained the value for L_0 (the heat of reaction at absolute zero) 38,055, so that the value of L_T , obtained from the expression † :

$$L_T = L_0 + \sigma'_v T + \sigma'' T^2$$

becomes $38,055 + 2.02T - 0.0031T^2$.

* The expressions used for the molecular heats of carbon dioxide and carbon monoxide are obtained from the formulæ given by Langen (*Dingl. polytech. J.*, 1903, 318, 433) for the mean thermal capacity of the gases over the range 0 to t° :

$$\text{For CO } C_v = 4.8 + 0.0006t$$

$$,, \text{ CO}_2 \quad C_v = 6.7 + 0.0026t.$$

† According to Kirchhoff's law the change in the value of the reaction heat with temperature depends on the difference between the molecular heats of the substances used up (factors) and of the substances formed (products) in the reaction. Adopting Haber's generalisation (*Thermodynamics of Technical Gas Reactions*, 1908, p. 27), if we imagine (1) the reaction to take place at the temperature T with a gain of heat L_T , and the resulting products to be then cooled down to absolute zero, we should obtain the same net amount of heat as though (2) we had first cooled the factors of the reaction to absolute zero and then allowed the reaction to proceed with a gain of heat, L_0 .

If $C_{y(0,T)}$ be the mean molecular heat of the products between 0° and T° , then the net gain of heat according to the first mode of procedure (1) would be $L_T + TC_{y(0,T)}$; and according to the second (2) it would be $L_0 + TC_{x(0,T)}$, where $C_{x(0,T)}$ is the mean molecular heat of the factors. Since these two quantities are equal :

$$L_T = L_0 + T(C_{x(0,T)} - C_{y(0,T)}).$$

The effect of temperature on the mean molecular heat of each substance can be expressed by the empirical formula :

$$C_v = a + bT + cT^2 + \dots$$

Only the first two constants, however, a and b , can be determined with any degree of accuracy, so that the mean thermal capacity of each substance taking part in the reaction must be represented by the approximation : $C_v = a + bT$. We can then write for the mean molecular heats of all the factors (all at constant volume) :

$$C_{factors} = \Sigma a + T \Sigma b,$$

and for the products :

$$C_{products} = \Sigma a^* + T \Sigma b^*.$$

Making use of Kirchhoff's law we get for the reaction heat at absolute zero the expression :

$$L_T - L_0 + T(\Sigma a - \Sigma a^*) + T^2(\Sigma b - \Sigma b^*).$$

If we call $\Sigma a - \Sigma a^*$ (the difference between the sum of the a 's of the factors and the sum of the a 's of the products), σ'_v , and $\Sigma b - \Sigma b^*$ (the difference between the sum of the b 's of the factors and the sum of the b 's of the products), σ'' , we get the formula $L_T = L_0 + \sigma'_v T + \sigma'' T^2$ used above. As Haber points out (*loc. cit.*, p. 49), the term σ'' does not need the index v , since it has the same value whether molecular heat at constant volume or constant pressure is meant.

In this calculation some uncertainty arises from the formula used for the atomic heat of carbon. It is obtained from the determinations made by Kunz (*Ann. Physik*, 1904, [iv], **14**, 327) for the mean specific heat of wood charcoal, as follow:

Between 0° and 435°	561°	728°	925°	1059°	1197°	1297°
$s = 0.243$	0.290	0.328	0.358	0.362	0.378	0.381

which find expression in the formula:

$$s = 0.2143 + 0.0001436t - 0.000000001975t^2.$$

Neglecting the last term, and changing to degrees absolute, we obtain the formula for the atomic heat used above.

In using this formula in the calculation of L_0 , however, it must be remembered that the specific heat of carbon decreases very rapidly at low temperatures, the specific heat of diamond at the interval -188° to -252° being, according to Dewar (*Proc. Roy. Soc.*, 1905, **76**, 325), as low as 0.0043. The value obtained for $L_0 = 38,055$ is therefore probably too high; but the relative values of L between 1073° and 1373° Abs. will not be greatly affected, and the correction should suffice to show to what extent the change in the value of L with temperature alters the value of the equilibrium constant.

Le Chatelier's formula, as applied to the system under consideration, can now be put in the form:

$$\frac{1}{2} \cdot \frac{38,055 + 2.02T - 0.0031T^2}{T} + \log_e P + \log_e \frac{C_1^2}{C_2} = k \dots (\text{ii}).$$

Whence, using the calculated values of C_1 and C_2 at atmospheric pressure given in the preceding table, we obtain:

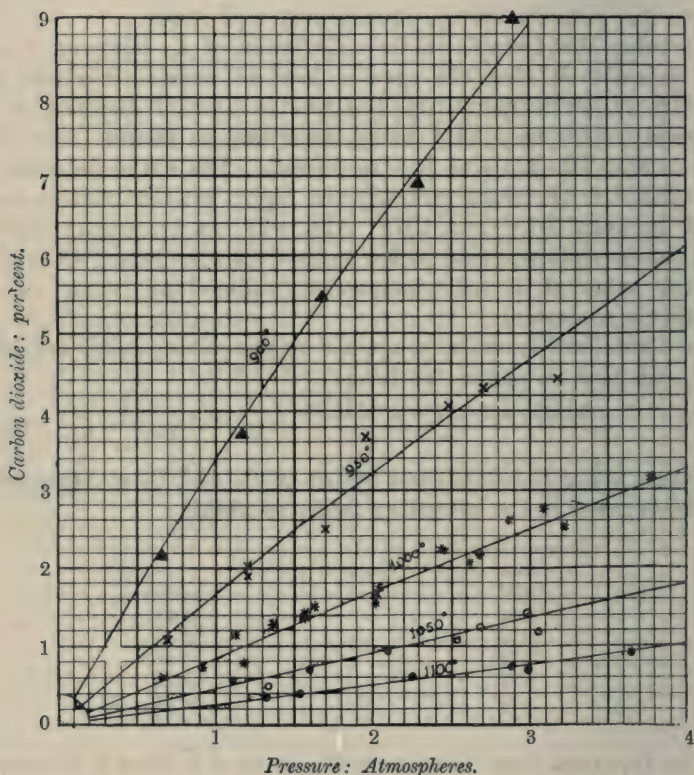
Temperature, Abs.	k .
1073	18.76
1123	18.75
1173	18.74
1223	18.74
1273	18.74
1323	18.74
1373	18.75

The apparent linear increase in the value of k when L is regarded as constant is therefore accounted for by the change in the value of L with temperature, and it is possible to apply a correction deduced from the known changes in the values of the specific heats of the reacting substances.

Whilst too great reliance cannot be placed on the value of the constant when approaching the limits of the system, it may be noted that the theoretical temperature at which the reaction $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ should be still appreciable is, at atmospheric pressure, about 588° Abs., at which temperature about 0.10 per

cent. of carbon monoxide should be formed. Boudouard, using finely divided nickel as catalyst, claims to have obtained complete dissociation of carbon monoxide at a temperature of 718° Abs., thereby implying that the reaction $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ is not reversible below that temperature. His observations are not confirmed, however, by Smitz and Wolff (*Zeitsch. physikal. Chem.*, 1903, **45**, 199), who, using a similar method of experiment, obtained distinct

FIG. 1.

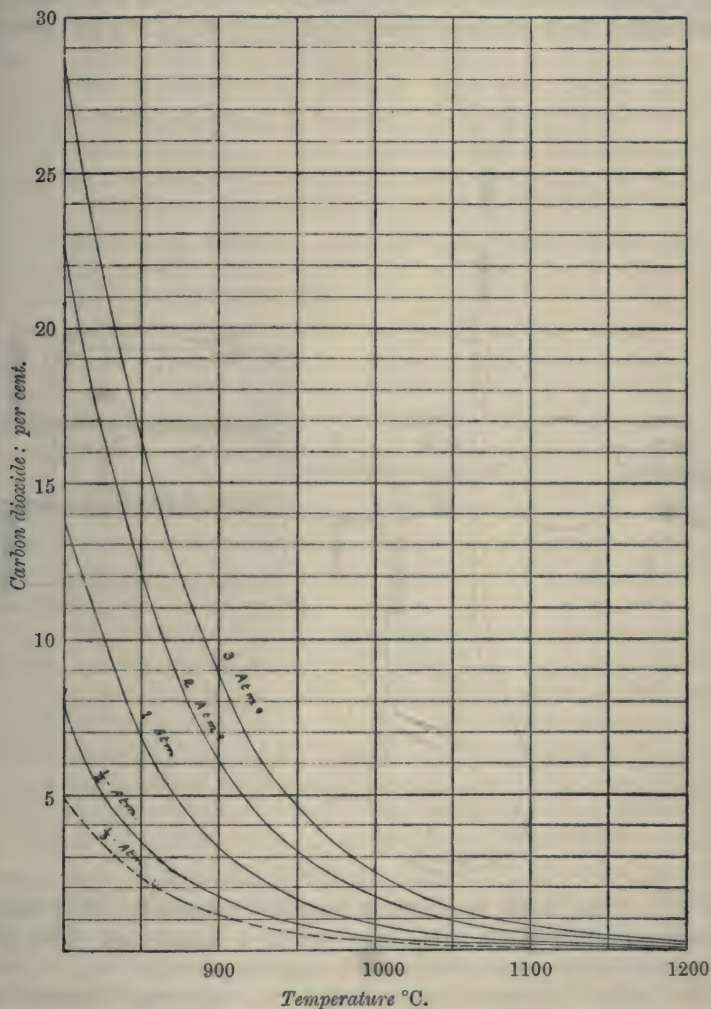


reversal at 718° Abs. Sabatier and Senderens (*Bull. Soc. chim.*, 1903, [iii], **29**, 294) state that total dissociation of carbon monoxide occurs at a temperature lying between 503° Abs. and 673° Abs.

The effect of pressure on the equilibrium at any one temperature is strictly in accordance with Le Chatelier's formula. If pressures in atmospheres are taken as ordinates and percentages of carbon dioxide as abscissæ, the points of intersection lie on a curve which at high temperatures is practically a straight line passing through

the origin. In Fig. 1 the results of our experiments are shown graphically in this manner, the curves being drawn through points calculated from equation (ii), and the values found by experiment being indicated by different symbols for each temperature.

FIG. 2.



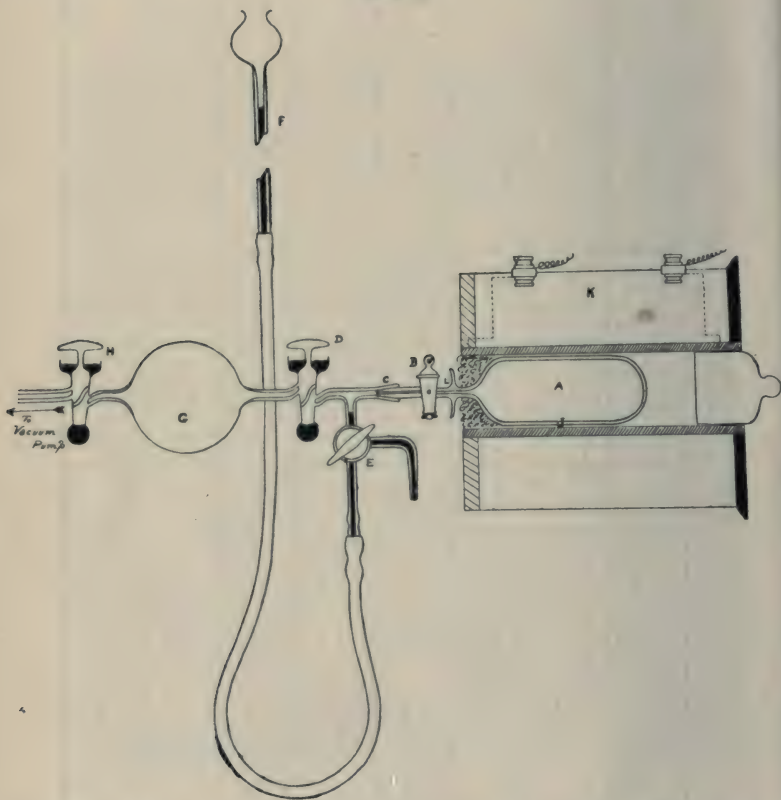
The curves in Fig. 2 show in a similar manner the variations in the percentages of carbon dioxide with temperature at 0.5, 1, 2, and 3 atmospheres pressure, as determined from our experiments; whilst we have added a curve for $\frac{1}{2}$ atmosphere, shown in dotted

line, calculated from equation (ii) and representing the effect of the passage of a slow current of air through excess of carbon.

EXPERIMENTAL.

The apparatus employed, which is shown diagrammatically in Fig. 3, consists essentially of a "reaction vessel" in the form of a stout-walled bulb of fused quartz (*A*), closed by a high pressure

FIG. 3.



tap (*B*) of the same material; a mercury manometer (*F*); and an exhausted glass globe (*G*), into which a sample of the gases contained in the quartz bulb can be rapidly passed.

The bulb is 11 cms. long and of 3 cms. external diameter, and has a capacity of about 52 c.c. when empty. It is one-third filled with purified wood-charcoal (prepared in the manner described in our previous paper), crushed, and sieved so as to pass through a 10-mesh sieve and remain on a 30-mesh. The weight of charcoal originally introduced into the bulb was 6 grams.

The quartz tap, which is of fine capillary bore, is fused as close as possible to the neck of the bulb, and makes connexion by means of a ground-joint (*C*) with a glass capillary T-piece. To one limb of this T-piece is fused a three-way tap (*E*), and to the other a mercury-cup tap (*D*) leading to the globe. The three-way tap communicates with the manometer, the side-tube admitting of the adjustment of the head of mercury to bring the short column to a constant level when measuring the pressure inside the bulb.

The bulb is heated in an electric resistance furnace (*K*), the refractory tube of which is wound with fine platinum wire, the coils at the end through which the neck of the bulb passes being placed close together to compensate for loss of heat by radiation from the furnace at that end, which is purposely left unprotected by heat-insulating material. This arrangement enables a zone of uniform temperature to be obtained throughout that portion of the furnace occupied by the bulb; that is to say, over a distance of 11 cms., starting 4 cms. from the mouth of the furnace. The "dead-space" between the bulb and the quartz tap amounts to less than 0.5 c.c., or about 1 per cent. of the total volume of the reaction vessel. The tap is kept cold by a rapid stream of water, which is prevented from entering the furnace by a quartz collar (*L*) fused to the neck of the bulb. The mouth of the furnace-tube is closed by tightly packed asbestos fibre.

Temperatures are measured by means of a platinum and platinum-rhodium thermo-couple passing along the bottom of the furnace tube, the junction being at *J*.

For the obtaining of a constant temperature during prolonged periods, a modification of the device described in our previous paper has been used (*loc. cit.*, p. 2185). This modification, which consists simply of the passage of the electric current through two sets of Nernst steadying resistances in series, has had the effect of ensuring a rigid maintenance of the experimental temperature during many days, and constitutes an improvement on our previous method.

Method of Conducting an Experiment:—The whole apparatus having been exhausted through the tap *H*, dried carbon dioxide or monoxide is introduced from a gas-holder, in which it has been stored during several days over concentrated sulphuric acid. The bulb containing the carbon is usually kept at a temperature of 200° whilst being filled, since below that temperature rapid absorption of the gas takes place. The tap *B* is then closed, and the remainder of the apparatus thoroughly exhausted. On now heating the furnace to the required experimental temperature, the expansion of the gas in the bulb creates a pressure which reaches from three to four atmospheres, dependent upon the temperature and pressure at

which it was filled, and on the amount of absorption that has been allowed to take place during filling.

After leaving a sufficient length of time for equilibrium to be established, the height of the mercury column required to balance the pressure in the quartz bulb is measured, tap *D* being closed and tap *B* opened to the previously exhausted T-piece. The pressure having been determined, tap *B* is closed, the T-piece re-exhausted, and, *B* having again been opened, a second pressure reading is taken. This mode of procedure has the effect of sweeping out the dead-space in the reaction vessel should the small quantity of gas contained therein have had insufficient time to diffuse; and it enables a correction to be applied for the reduction of pressure in the reaction vessel when it is first opened to the exhausted T-piece (the capacity of which is about 1 c.c.), the pressure-reading required being that existing in the bulb before tap *B* is first opened.

A sample of the gases is obtained by momentarily turning the tap *D* on to the exhausted globe. In this manner the sample is instantaneously cooled below the temperature at which reaction can take place, and the pressure in the reaction vessel is reduced. The whole of the sample in the globe is then withdrawn through a mercury vacuum pump and analysed.

The volume of gas allowed to escape into the globe from the reaction vessel has usually been sufficient to reduce the pressure in the latter by about half an atmosphere. Heating is then continued at this lower pressure during a sufficient length of time to re-establish equilibrium, and a second sample then taken in a similar manner. In this way from five to seven samples of gas are obtained from the reaction vessel, representing the quantities of carbon dioxide and monoxide in equilibrium over carbon at the same temperature, but at pressures varying from 3 to 0.5 atmospheres.

As an example, to render the mode of operation clear, we may quote the details of experiment No. P 20.

Equilibrium Temperature = 1000°.

The reaction vessel was filled at a temperature of 300° and at 750 mm. pressure, and the temperature then raised to 1000°.

Sample 1.—After heating during twelve hours at 1000°,
 $P = 748 + 1700 = 2448$ mm. = 3.22 atmospheres.

Analysis: $\text{CO}_2 = 2.52$ per cent.*
 $\text{CO} = 97.48$ „

* The percentages are in all cases calculated as those of the "nitrogen-free" gases. The gases usually contained from 1 to 2 per cent. of nitrogen.

Sample 2.—After further heating during six hours at 1000° ,
 $P = 750 + 1240 = 1990$ mm. = $2\cdot62$ atmospheres.

Analysis: $\text{CO}_2 = 2\cdot06$ per cent.
 $\text{CO} = 97\cdot94$ „

Sample 3.—After further heating during six hours at 1000° ,
 $P = 752 + 800 = 1552$ mm. = $2\cdot05$ atmospheres.

Analysis: $\text{CO}_2 = 1\cdot75$ per cent.
 $\text{CO} = 98\cdot25$ „

Sample 4.—After further heating during twelve hours at 1000° ,
 $P = 754 + 425 = 1179$ mm. = $1\cdot56$ atmospheres.

Analysis: $\text{CO}_2 = 1\cdot36$ per cent.
 $\text{CO} = 98\cdot64$ „

Sample 5.—After further heating during six hours at 1000° ,
 $P = 753 - 53 = 700$ mm. = $0\cdot93$ atmosphere.

Analysis: $\text{CO}_2 = 0\cdot72$ per cent.
 $\text{CO} = 99\cdot28$ „

We give below all the determinations that have been made at different temperatures and pressures, arranging them for convenience in tabular form in order of decreasing pressure. The values of k are calculated from equation (ii).

A series of experiments at each temperature was preceded by several preliminary trials made to determine the length of time that should be allowed for equilibrium to be established.

Temperature 800° .

Pressure. Atms.	CO_2 per cent.	CO per cent.	k .
3 05	28 40	71 60	18 78
2 57	26 45	73 55	18 74
2 10	22 85	77 15	18 78
1 75	21 75	78 25	18 68
1 23	16 12	83 88	18 75
Mean value of k			18 75

Temperature 900° .

2 90	9 05	90 95	18 69
2 30	6 92	93 08	18 77
1 66	5 47	94 53	18 71
1 17	3 70	96 30	18 79
0 65	2 17	97 80	18 78
Mean value of k			18 75

Temperature 950°.

Pressure. Atms.	CO ₂ per cent.	CO per cent.	<i>k</i> .
3·18	4·42	95·58	18·85
2·71	4·32	95·68	18·72
2·48	4·07	95·93	18·69
1·95	3·69	96·31	18·56
1·69	2·50	97·50	18·83
1·21	2·04	97·96	18·78
1·21	1·90	98·10	18·71
0·69	1·11	98·89	18·78
Mean value of <i>k</i>			18·74

Temperature 1000°.

3·78	3·17	96·83	18·70
3·22	2·52	97·48	18·79
3·08	2·77	97·23	18·65
2·86	2·59	97·41	18·64
2·67	2·18	97·82	18·75
2·62	2·06	97·94	18·79
2·45	2·24	97·76	18·64
2·43	2·24	97·76	18·63
2·05	1·75	98·25	18·72
2·02	1·63	98·37	18·77
2·02	1·55	98·45	18·83
1·63	1·52	98·48	18·63
1·56	1·44	98·56	18·64
1·56	1·36	98·64	18·71
1·36	1·30	98·70	18·61
1·17	0·79	99·21	18·97
1·14	1·17	98·83	18·55
0·93	0·72	99·28	18·84
0·66	0·65	99·35	18·60
Mean value of <i>k</i>			18·71

Temperature 1050°.

3·06	1·17	98·83	18·89
2·99	1·42	98·58	18·67
2·68	1·25	98·75	18·69
2·54	1·06	98·94	18·80
2·09	0·92	99·08	18·76
1·59	0·71	99·29	18·75
1·34	0·47	99·53	18·99
1·11	0·58	99·42	18·59
0·83	0·52	99·48	18·52
Mean value of <i>k</i>			18·74

Temperature 1100°.

3·64	0·92	99·08	18·71
2·98	0·68	99·32	18·82
2·87	0·73	99·27	18·71
2·25	0·60	99·40	18·67
1·53	0·39	99·61	18·72
1·33	0·35	99·65	18·68
Mean value of <i>k</i>			18·72

Equilibrium is reached rapidly at the higher temperatures under the conditions of these experiments, but at 800° it is only attained after heating during seventy-two to ninety-six hours. At 700° the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ is extremely slow, experiments in which the gases were maintained at atmospheric pressure, by allowing release through the side-tube of the tap *E* (Fig. 3) dipping under mercury, only resulting in the formation of 18 per cent. of carbon dioxide after five days' heating.

This work has been undertaken in connexion with the experiments carried out by the Mining Association of Great Britain on coal-dust explosions, and forms part of an investigation into the mode of combustion of carbon.

ALTOFTS.

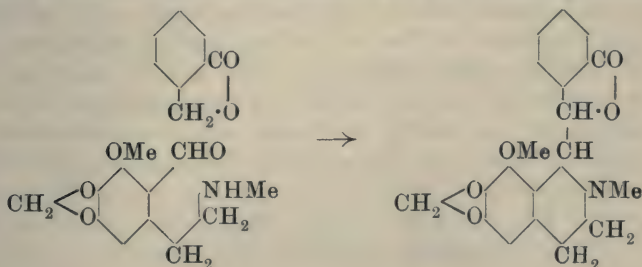
CXXIII.—*Synthetical Experiments in the Group of the isoQuinoline Alkaloids. Part I. Anhydrocotarninephthalide.*

By EDWARD HOPE and ROBERT ROBINSON.

DURING the course of a systematic investigation concerning the reactions of substances of the type of cotarnine, the authors have observed the great facility with which such aldehyde imines condense with nitro-compounds, and in the present communication an account is given of the way in which this property may be utilised for the synthesis of an alkaloid of the type of narcotine and hydrastine.

The synthesis of gnoscopine (*dl*-narcotine or anhydrocotarnine-meconine) (Perkin and Robinson, this vol., p. 775) was effected by the condensation of cotarnine with meconine, and in a similar manner *anhydrocotarninephthalide* is produced by boiling an alcoholic solution of cotarnine with phthalide.

The reaction occurs in accordance with the following scheme:



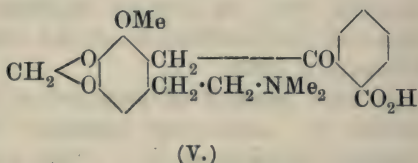
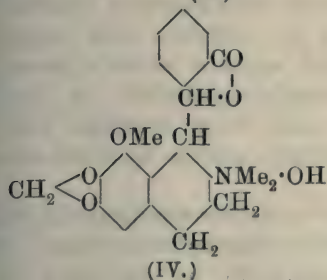
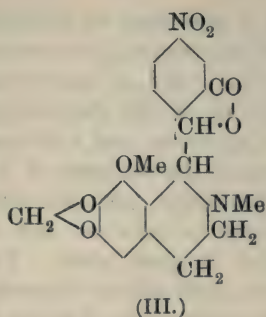
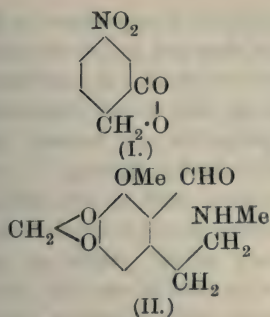
It was pointed out in the communication already referred to (Perkin and Robinson, *loc. cit.*) that the yield of gnoscopine produced by the direct condensation of cotarnine and meconine is very small; when phthalide is substituted for meconine the yield is somewhat better, and as the process can be carried through quickly it is an advantageous one for the rapid preparation of small quantities of anhydrocotarninephthalide.

A short time ago the authors (Proc., 1910, **26**, 228) discovered that nitromeconine condenses with cotarnine with much greater facility than meconine itself, and in the present instance a similar observation has been made, since our experiments have shown that the introduction of a nitro-group into phthalide enormously increases the ease with which this substance enters into reaction with cotarnine.

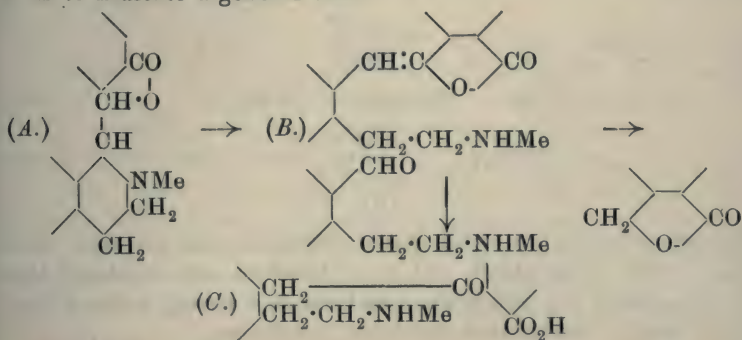
The whole question of the mechanism of the reaction involving the production of condensation products of cotarnine with nitro-compounds will, it is hoped, be discussed when some experiments which we have made bearing directly on this problem are published. In the meantime we desire to point out that the imino-group of cotarnine is certainly an important factor, and probably in two ways; first in attracting the nitro-compound and in forming a loose combination of the type of the compounds obtained from amines and trinitrobenzene, and secondly, in effecting the condensation between the aldehyde and methylene groups in a manner similar to that in which secondary bases are active in Knoevenagel's reaction. A further very important consideration arises from the fact that the aldol condensation, which is doubtless the first stage in the reaction, loses water with the formation of a closed chain *N*-methyltetrahydroisoquinoline derivative; so that we have to deal with an irreversible reaction, and this is no doubt the chief cause of the good yields which are obtained.

The importance of these observations on the reactivity of nitrophthalides is, from a synthetical point of view, very much enhanced by the fact that it is possible to replace the nitro-group successively by the amino- and hydrazino-groups, and finally by a hydrogen atom. Very good yields are obtained in these reactions, and it is probable that they represent the best way of synthesising substances of the type of narcotine and hydrastine. The results that have been obtained in the present case are briefly summarised as follows.

Cotarnine (I) is readily condensed with 5-nitrophthalide (II) in alcoholic solution, the product being the base, *anhydrocotarnine-5-nitrophthalide* (III), and this is obtained in practically quantitative yield. The properties of this nitroamine are described in detail in the experimental portion of this paper (see p. 1157), but



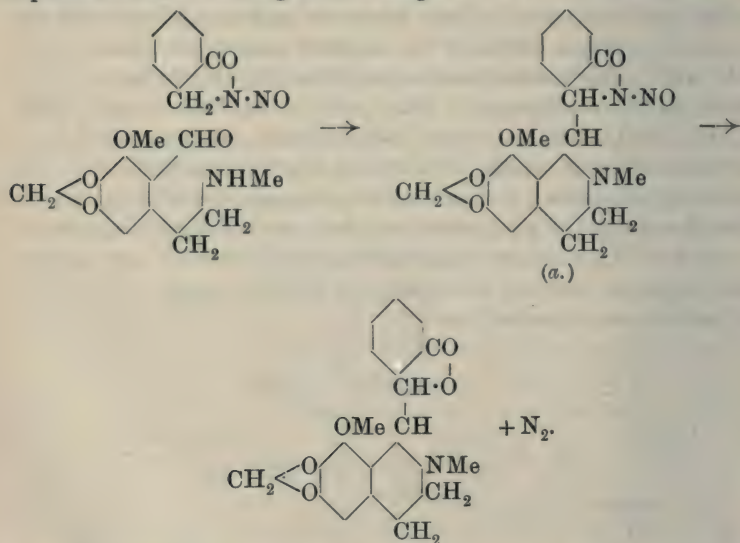
its decomposition on warming with glacial acetic acid into cotarnine and 5-nitrophthalide calls for some remark. Narcotine itself suffers a similar hydrolytic scission into cotarnine and meconine under the same conditions, and although the reaction occurs very much more readily with anhydrocotarnine-5-nitrophthalide, there can be little doubt that the mechanism is the same in the two cases. Rabe (*Ber.*, 1907, **40**, 3280) has found that narcotine, under the influence of dilute acetic acid, yields, in addition to cotarnine and meconine, an imino-ketone termed nornarceine, the decomposition being similar to that involving the production of cinchotoxine from cinchonine. The course of the reactions under discussion is probably represented by the following scheme, in which the benzene rings are written so as to indicate a general case:



A is a substance of the type of narcotine, *B* represents a hypothetical intermediate compound which is changed in two directions; on the one hand, a substance like nornarceine (*C*) is produced by the opening of the phthalide ring, and on the other, cotarnine or similar substance and a derivative of phthalide are formed by the addition of the elements of water to the double linking.

On treatment with tin and hydrochloric acid in the cold, the nitroamine is reduced, and *anhydrocotarnine-5-aminophthalide* is produced in good yield. This primary amine yields an *acetyl* derivative and may be diazotised, and a hydrazine may be obtained from the diazonium chloride by reduction with stannous chloride. By elimination of the hydrazino-group by oxidation with copper sulphate, a product is obtained which appears to be a stereoisomeric modification of anhydrocotarninephthalide, a base identical with the original substance only being obtained after repeated recrystallisation of the sparingly soluble hydrochloride (compare p. 1165).

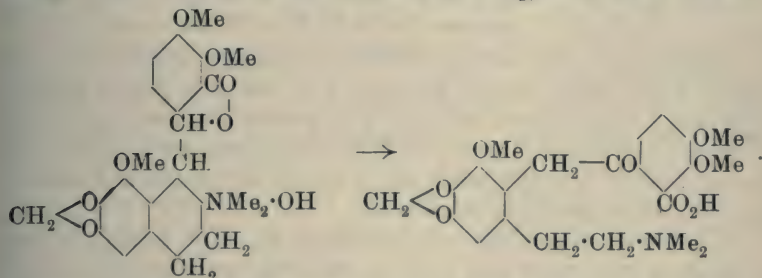
A third method of preparation of anhydrocotarninephthalide consists in condensing cotarnine with nitrosophthalimidine in alcoholic solution at 0°. This result is to be explained in accordance with the following scheme, in which the reaction is represented as occurring in two stages:



Nitrosophthalimidine itself yields phthalide and nitrogen when warmed with dilute alkali, and it is therefore not unnatural that the nitroamine (*a*), which also functions as a strong tertiary base, should suffer a similar decomposition in solution.

Anhydrocotarninephthalide shows in its behaviour towards reagents the greatest analogy to narcotine; for example, on oxidation with dilute nitric acid, it yields cotarnine and phthalaldehydic acid, whilst narcotine, under similar treatment, yields cotarnine and opianic acid, that is to say, dimethoxyphthalaldehydic acid.

Again, narcotine methyl hydroxide, on boiling with water, is changed into narceine, and the reaction is represented as follows:



It is interesting that in a similar way a dedimethoxynarceine may be obtained from anhydrocotarninephthalide.

The methiodide of the latter base yields on warming with silver chloride in aqueous solution the corresponding methochloride, from which, by the action of alkalis, anhydrocotarninephthalide methyl hydroxide (IV) is precipitated. On boiling with water, a clear solution is obtained, from which dedimethoxynarceine (V) crystallises after concentration and cooling.

The substance is quite similar to narceine in its reactions (compare p. 1169), and its formation is the most convincing proof of the correctness of the structure assigned to anhydrocotarninephthalide.

EXPERIMENTAL.

Anhydrocotarnine-5-nitrophthalide (Formula III, p. 1155).

The condensation leading to the production of this substance is best conducted as follows.

Cotarnine (20 grams) is dissolved in alcohol (100 c.c.), and 5-nitrophthalide (16 grams) (Hoenig, *Ber.*, 1885, **18**, 3447) added to the mixture. On gently heating, the nitrophthalide, although sparingly soluble in alcohol, quickly dissolves, forming a peculiar, greenish-violet solution, from which a yellow, granular, crystalline precipitate begins to separate after three or four minutes. The liquid is boiled during ten minutes, then cooled, and the condensation product collected and washed with alcohol. After drying in a steam-oven, the substance is found to be perfectly pure, whilst the yield is so good that from 70 grams of nitrophthalide 125 grams of the base are obtained.

The substance is very sparingly soluble in methyl and ethyl alcohols, ethyl acetate, or ether.

It is comparatively readily soluble in chloroform, and may be easily recrystallised from a mixture of chloroform and ethyl alcohol. The crystals are very pale yellow prisms, which melt at 176—177°, and decompose to a red liquid:

0.1135 gave 0.2527 CO_2 and 0.0484 H_2O . $\text{C}=60.7$; $\text{H}=4.7$.

$\text{C}_{20}\text{H}_{18}\text{O}_7\text{N}_2$ requires $\text{C}=60.3$; $\text{H}=4.8$ per cent.

Anhydrocotarnine-5-nitrophthalide is readily soluble in cold glacial acetic acid, and on dilution with water a yellow solution is obtained, from which ammonia precipitates the unchanged base. A similar behaviour is found with dilute mineral acid, except that the solution of the hydrochloride is almost colourless, and after a time deposits a sparingly soluble salt.

If, however, the solution in glacial acetic acid is boiled, then on dilution with water and cooling, colourless crystals are obtained, which are found to melt at 143° and to consist of 5-nitrophthalide. The filtrate from the nitrophthalide gives, on the addition of aqueous picric acid, a picrate which melts at 141—143°, and possesses all the characteristics of cotarnine picrate (Salway, Trans., 1910, 97, 1209).

The pale yellow solution of the base in concentrated sulphuric acid becomes blood-red when a small trace of nitric acid is added to it. This reaction is shown by all condensation products and alkaloids which yield cotarnine on oxidation, and therefore by all the substances described in this communication.

Anhydrocotarnine-5-nitrophthalide picrate is produced as a yellow precipitate when picric acid in aqueous solution is added to the base dissolved in dilute acetic acid. The dried substance is readily crystallised from a mixture of acetone and methyl alcohol, and consists of exceedingly small, yellow prisms, melting at 159—161°.

A solution of the base in dilute hydrochloric acid gives precipitates of double salts with the usual reagents.

The *platinichloride* is a pale yellow, amorphous substance, which becomes crystalline on keeping; the *aurichloride* is a buff precipitate produced in very dilute solutions; the *mercurichloride* is colourless and crystalline. These derivatives resemble in appearance the corresponding compounds from narcotine.

This nitro-base was found to be difficult to combine with methyl iodide. It was recovered unchanged after boiling with the iodide, alone, with alcohol, or in chloroform solution. In one experiment a small quantity of a substance containing iodine was also isolated. This was sparingly soluble, and melted and decomposed at 193—195°.

Anhydrocotarnine-5-aminophthalide,
 $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}(\text{OMe})\cdot\text{C}_4\text{H}_3\text{N}\cdot\text{C}_2\text{HO}_2\cdot\text{C}_6\text{H}_3\cdot\text{NH}_2.$

A considerable number of experiments have been made in the effort to discover the conditions under which anhydrocotarnine-5-nitrophthalide is best reduced to the corresponding amine, and ultimately the following procedure was adopted.

It is inadvisable to employ more than the stated quantities in one experiment.

Anhydrocotarnine-5-nitrophthalide (10 grams) was dissolved in glacial acetic acid (40 c.c.), and to the solution, granulated tin (5 grams) and hydrated stannous chloride (22 grams), dissolved in concentrated hydrochloric acid (40 c.c.), was quickly added. The reaction mixture will become hot if allowed to remain, but the temperature was kept at 15—18° by cooling in running water.

After four hours the original yellow colour had almost disappeared, and the liquid was poured into water (800 c.c.).

A colourless precipitate, probably a stannichloride, which was at first produced redissolved in the excess of water, and the clear liquid was decanted from the undissolved tin and rendered alkaline by the addition of a large excess of potassium hydroxide. This must be free from carbonate, and was added all at once. In carrying out a series of reductions, potassium hydroxide (1400 grams) was dissolved in two litres of water, and 200 c.c. were used for each experiment. The colourless precipitate was nearly free from tin, and in some experiments was separated by filtration and recrystallised from chloroform and alcohol; it was found, however, to be more advantageous to extract at once with chloroform as soon as the alkali was added. The chloroform solution was dried with potassium carbonate and distilled. When crystallisation of the amine commenced, methyl alcohol was added, and the liquid cooled. The sandy, crystalline powder was separated by filtration, washed with alcohol, and dried. The yield was 53 grams of the pure amine from 60 grams of the nitro-compound.

The substance crystallises well when its chloroform solution is mixed with alcohol, and forms long, flat prisms. It is readily soluble in chloroform or pyridine, moderately so in ethyl alcohol, ethyl acetate, or acetone, and very sparingly soluble in benzene, ether, or methyl alcohol.

The pure amine is quite colourless, and melts at 220—221° when heated not too slowly; a certain amount of decomposition appears to take place above 190°:

0.1301 gave 0.3085 CO_2 and 0.0666 H_2O . $\text{C} = 64.7$; $\text{H} = 5.7$.

0.1767 „ 0.4206 CO_2 „ 0.0873 H_2O . $\text{C} = 64.9$; $\text{H} = 5.1$.

$\text{C}_{20}\text{H}_{20}\text{O}_5\text{N}_2$ requires $\text{C} = 65.2$; $\text{H} = 5.4$ per cent.

The salts of this compound are readily soluble in water.

The *platinichloride* is a very pale yellow precipitate, soluble in hot water; and the *picrate* is bright yellow, and sparingly soluble. When heated in glacial acetic acid solution, this base, unlike the corresponding nitro-compound, does not suffer decomposition, and may be recovered unchanged.

With sulphuric acid and a trace of nitric acid, a blood-red colour is produced, rapidly changing through orange to yellow.

Diazotisation of the amino-group is readily effected; the addition of an excess of *isoamyl* nitrite to the alcoholic solution of the base in alcoholic sulphuric acid produces a pale yellow precipitate of a diazonium salt. The solution in water changes very rapidly, even at 0°, from pale yellow to intense red, but we have been unable to isolate any phenolic base or other substance from the products of decomposition. The inconvenience caused by this instability of the diazonium chloride in aqueous solution is entirely obviated by operating in concentrated hydrochloric acid, when a diazo-solution is obtained, which can be kept in a freezing mixture for an hour without decomposition. An intense carmine azo-colouring matter is obtained by coupling this diazonium chloride with β -naphthol in alkaline solution, whilst with "R salt" under the same conditions a beautiful crimson dye, which shows intense blue fluorescence, is produced. These azo-compounds dissolve in sulphuric acid to a royal blue solution, which becomes violet and then red on dilution with water.

Combination also takes place, in the presence of a small excess of acid, with diethylaniline, a deep orange-red colour being formed.

Anhydrocotarnine-5-acetylaminophthalide.

In preparing this substance, it was found to be advisable to carry out the reaction without the application of heat.

The pure amino-compound was shaken with enough acetic anhydride to dissolve it, when acetylation took place with a small rise in temperature. The liquid was poured into water, and, when all the acetic anhydride had been decomposed, rendered alkaline with ammonia. A white precipitate of the acetylmino-compound was produced, and, after collecting and drying, the substance was crystallised from methyl alcohol, in which it is sparingly soluble. It consists of small, elongated prisms, melting and decomposing at 247°. The substance is not attacked by nitrous acid, and forms soluble salts with acids, from solutions of which the usual alkaloidal reagents produce precipitates.

For analysis, the substance was dried in a vacuum over sulphuric acid:

- (A) 0.1629 gave 0.3786 CO₂ and 0.0899 H₂O. C=63.4; H=6.1.
 (B) 0.1238 „ 0.2894 CO₂ „ 0.0671 H₂O. C=63.7; H=6.0.
 (C) 0.1048 „ 0.2490 CO₂ „ 0.0530 H₂O. C=64.8; H=5.6.

C₂₂H₂₂O₆N₂ requires C=64.3; H=5.3 per cent.

C₂₂H₂₂O₆N₂.CH₄O requires C=62.4; H=5.9 per cent.

Specimens of this substance were occasionally obtained melting at 164°, although on recrystallisation the melting point rose to 245°. Analysis *A* was of such a specimen; *B* melted at 240°, and was prepared by heating the amine with acetic anhydride; *C* melted at 248°, and was obtained as described above. The low values obtained for carbon in *A* and *B* are probably to be ascribed to methyl alcohol of crystallisation partly driven off.

Anhydrocotarnine-5-iodophthalide,
 CH₂:O₂:C₆H(OMe):C₄H₈N.C₂HO₂:C₆H₃I.

Anhydrocotarnineaminophthalide (5 grams) is dissolved in concentrated hydrochloric acid (30 c.c.), cooled to 0° in a freezing mixture, and treated with saturated sodium nitrite solution until a test portion diluted with water shows immediate reaction with starch and potassium iodide. The orange solution is then poured all at once into water (200 c.c.) containing potassium iodide (20 grams). The evolution of nitrogen which results is accompanied by considerable frothing, and the small excess of nitrite liberates a certain amount of iodine. The free iodine is removed by passing a stream of sulphur dioxide through the liquid. A sparingly soluble pale yellow precipitate of the hydriodide of the base remains. Ammonia is added, and the solids collected and washed with water. The substance is crystallised from ethyl alcohol, to which some ammonia is added to ensure the decomposition of the hydriodide. It is finally crystallised from methyl alcohol, and is obtained in colourless, shining spangles, melting at 173°, with slight previous softening. Under the microscope, the crystals are seen to be small, hexagonal plates. It is sparingly soluble in methyl alcohol or ether, but readily so in hot ethyl alcohol:

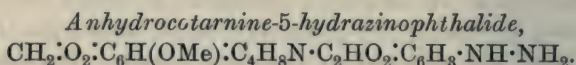
0.1265 gave 0.2346 CO₂ and 0.0452 H₂O. C=50.6; H=3.9.

0.1232 „ 0.0609 AgI. I=26.7.

C₂₀H₁₈O₅NI requires C=50.3; H=3.8; I=26.5 per cent.

The *hydrochloride* and *sulphate* of this base are sparingly soluble in cold water. The *platinichloride* is an almost colourless, amorphous precipitate; the *aurichloride* is pale yellow. These compounds are precipitated in very dilute solutions. A *mercurichloride* is obtained as a white, amorphous precipitate, which becomes crystalline on keeping. An attempt to prepare the methiodide of

this base resulted in a substance that was probably the *hydriodide*, since, after treatment with silver chloride in aqueous solution, the addition of alkali to the filtered liquid gave a precipitate, which crystallised from alcohol in hexagonal plates, and melted at 171—173°. The melting point was not lowered when the substance was intimately mixed with an equal quantity of anhydrocotarnineiodophthalide.



This hydrazine is prepared by the reduction of diazotised anhydrocotarnine-5-aminophthalide according to the following method, which in our experience cannot be varied in any important particular.

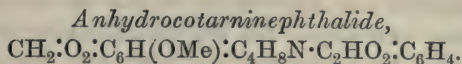
Anhydrocotarnine-5-aminophthalide (6 grams) was dissolved in concentrated hydrochloric acid (60 c.c.), and treated with a solution of sodium nitrite, until a diluted test portion immediately liberated iodine from potassium iodide, the temperature being kept below 8° by cooling in ice-water.

To the diazo-solution was added hydrated stannous chloride (20 grams), dissolved in concentrated hydrochloric acid (30 c.c.), when reduction was found to occur at once, and a colourless precipitate, probably consisting of the stannichloride of the hydrazine, separated in a crystalline condition. The solid was collected, dissolved in water, and decomposed with sodium carbonate. Potassium or sodium hydroxides must not be employed here, because the lactone ring of the base appears to suffer ready hydrolysis. The precipitate was collected, washed with water, and extracted with boiling alcohol. The addition of water to the hot alcoholic filtrate causes the crystallisation of the hydrazine. The substance is readily soluble in hot ethyl alcohol, and is best recrystallised from methyl alcohol. It forms colourless needles, which melt and decompose at 113—116°:

0.1163 gave 11.0 c.c. N_2 at 12° and 751 mm. $\text{N} = 11.2$.

$\text{C}_{20}\text{H}_{21}\text{O}_5\text{N}_3$ requires $\text{N} = 10.9$ per cent.

Benzylidene Derivative.—Molecular proportions of this hydrazine derivative and benzaldehyde were heated together for a few minutes in methyl-alcoholic solution. A sparingly soluble substance quickly crystallised on cooling. After recrystallisation from ethyl acetate, it formed pale yellow prisms, melting at 230—232°. The substance is soluble in dilute acids, and yields a bright yellow *picrate*.



Three methods have been developed for the synthesis of this alkaloid, a substance of considerable interest, in that it is *dedimethoxygnoscopine*.

(a) By Direct Condensation of Cotarnine with Phthalide.

The preparation of anhydrocotarninephthalide by this method is a comparatively simple matter, and although the yield is not good, yet it is better than that obtained when meconine replaces the phthalide (compare Perkin and Robinson, this vol., p. 782). A solution of phthalide (20 grams) in methyl alcohol (100 c.c.) was treated with cotarnine (15 grams), and the mixture boiled during three hours. The orange-yellow solution was then poured into water, and rendered acid to Congo-red with hydrochloric acid. The excess of phthalide was then removed by extraction with ether, and the aqueous layer separated. A large amount of sodium acetate was added so as to liberate the base, which was extracted with ether. The ethereal solution was yellow, but became almost colourless after repeated washing with water. It was dried with potassium carbonate, and, after removal of the solvent, the base remained as a viscid, colourless oil, which quickly crystallised in contact with methyl alcohol. After being recrystallised several times from the same solvent, it was obtained in colourless, shining needles, which were proved to be identical with anhydrocotarninephthalide obtained in (b) and (c). The melting point was 200—201°, and the temperature was unaltered by admixture with an equal quantity of the base from method (b).

It is important to notice that no appreciable condensation occurs between cotarnine and phthalide in the cold. Otherwise it might be imagined that the reaction immediately to be described owes its success to the production of phthalide from the nitroso-compound, and subsequent condensation with cotarnine. That this is not the case is also indicated by the increased yield of product obtained from nitrosophthalimidine.

(b) Condensation of Cotarnine with Nitrosophthalimidine.

A solution of cotarnine (23 grams) in ethyl alcohol (100 c.c.) was poured on nitrosophthalimidine (16 grams) contained in a flask which was immersed in ice-water; if this precaution is not observed, the rise in temperature consequent on the reaction causes a considerably diminished yield of the desired product. After a few

hours, the mixture was allowed to remain at the ordinary temperature during two days. As the condensation proceeded, the colour became a little darker, and nitrogen was continuously evolved. The clear orange-yellow solution was decanted from the small quantity of nitrosophthalimidine which remained undissolved, and heated to the boiling point for two or three minutes. The cooled liquid was poured into six times its volume of water, when a sticky, yellow precipitate was formed, and adhered to the sides of the containing vessel. The aqueous solution was decanted, and the residue treated with boiling dilute hydrochloric acid, in which all was soluble but a small quantity of oily matter. After filtration and cooling, a further quantity of oil separated, and from this the pale yellow solution was decanted. On keeping overnight in the ice-chest, a large quantity of colourless crystals was obtained, and these were found to consist of the hydrochloride of anhydrocotarninephthalide; further crops were obtained from the mother liquors. The substance crystallises from water in hexagonal plates, but if the concentrated solution is quickly cooled, then rather more indefinite prisms result.

This hydrochloride (Found, N=2.9 per cent.) appears to give up water of crystallisation at 120°, and then melts to a red liquid at 231—232°. The salt was dissolved in warm water, and decomposed with ammonia, when a white, flocculent precipitate was produced. Sometimes if the hydrochloride was not very pure, or the temperature was too high, the base was obtained in a sticky condition, soon hardening, however, in contact with cold water. In either case the substance crystallised well from methyl alcohol in long, colourless needles or prisms, melting at 201°:

0.1098 gave 0.2726 CO₂ and 0.0545 H₂O. C=67.7; H=5.5.

0.1266 „ 0.3171 CO₂ „ 0.0697 H₂O. C=68.3; H=6.1.

0.1251 „ 4.9 c.c. N₂ at 19° and 734 mm. N=4.3.

C₂₀H₁₉O₅N requires C=68.0; H=5.4; N=3.9 per cent.

(c) *Oxidation of Anhydrocotarnine-5-hydrazinophthalide.*

It is fortunate for the success of this experiment that although substances of the type of narcotine are very easily oxidised, and even by such agents as ferric chloride and platinic salts, yet they are not attacked by copper sulphate, and consequently the usual oxidation method can be applied to the hydrazine derivative already described (see p. 1162).

Anhydrocotarnine-5-hydrazinophthalide (4 grams) was dissolved in rather more than the necessary amount of dilute acetic acid, and heated to 50°. A solution (20 c.c.) of copper sulphate, saturated

at the room temperature, was now added, and oxidation was found to occur quickly, accompanied by the evolution of nitrogen and the separation of cuprous oxide. The mixture was allowed to remain until no more bubbles of gas were produced—a condition best determined by listening to the sound caused by the disengaged nitrogen. After the addition of hydrochloric acid, the copper was completely removed by means of hydrogen sulphide. The colourless filtrate was allowed to remain in the cold, when it gradually deposited a quantity of colourless, glistening crystals, which consisted of a sparingly soluble hydrochloride. This was separated by filtration, and the filtrate basified with ammonia, thus producing a grey precipitate, which, after drying, was extracted with ether in a Soxhlet apparatus. The residue remaining after evaporation of the ether was again converted into hydrochloride, and purified by the recrystallisation of this salt from water. The two quantities of hydrochloride thus obtained were found to be identical, and to consist of the hydrochloride of anhydrocotarninephthalide. The substance crystallised from water in hexagonal plates, lost water of crystallisation at 120° , and then melted at about 230° .

After several recrystallisations the salt was decomposed with ammonia, and the resulting base crystallised from methyl alcohol, when it was produced in long, colourless prisms, melting at $200\text{--}201^{\circ}$. The identity of the base with anhydrocotarninephthalide from (b) was proved by the fact that an intimate mixture of the two substances also melted at 200° .

Now, although it is quite clear that by using the process of purification through the hydrochloride, as described above, anhydrocotarninephthalide results; yet it is in our opinion probable that the direct product of the oxidation of the hydrazine is a different substance, namely, a stereoisomeric β -anhydrocotarninephthalide.

When the liquid, after the oxidation of the hydrazino-base with copper sulphate, is treated with an excess of sodium acetate, and extracted with ether, a colourless solution is obtained, which, after drying with potassium carbonate and removal of the ether, leaves a white, crystalline crust. The substance in this condition is very soluble in ethyl alcohol, but can be crystallised from methyl alcohol. The crystals are not very definite in shape, but they seem to melt sharply at 180° . It is very difficult, however, to prove that this is not merely an impure specimen of the ordinary form of the alkaloid.

A specimen of hydrochloride which had been obtained by the oxidation of the hydrazine, and crystallised only once, was basified, and gave, on crystallisation from methyl alcohol, a substance melting at $181\text{--}184^{\circ}$, with previous softening at 171° . A second

crystallisation raised the melting point to 192—195°, with softening at 176—180°:

0.1245 gave 0.3080 CO₂ and 0.0623 H₂O. C=67.7; H=5.5.

0.1563 „ 6.0 c.c. N₂ at 18° and 736 mm. N=4.3.

C₂₀H₁₉O₅N requires C=68.0; H=5.4; N=3.9 per cent.

This alkaloid of low melting point, if it is anhydrocotarninephthalide, must contain a considerable quantity of impurity, since it is our experience that one crystallisation of anhydrocotarninephthalide, from (a) or (b), always results in a product which has the characteristic appearance of this base, however crude the material may be, whilst the substance melting at 192° does not acquire the same appearance by crystallisation only, but must be again converted into the hydrochloride. If this be granted, then the analysis may be taken to show that the impurity has the same percentage composition as anhydrocotarninephthalide. That it has the same chemical properties is proved by the fact that we have made the experiment on the oxidation with dilute nitric acid, and on the conversion to dedimethoxynarceine, with the supposed stereoisomeric base, and with results identical with those described in the ensuing sections.

Anhydrocotarninephthalide, as already mentioned, crystallises well from methyl alcohol or ether, and occurs in long prisms which are hexagonal in shape. The melting point of the purest specimens was 201—202°, without decomposition. The solution of the sparingly soluble hydrochloride gives with the usual reagents precipitates, none of which is very characteristic in appearance. The *platinichloride* is formed as an almost colourless, insoluble amorphous precipitate:

0.1440 gave 0.0256 Pt. Pt=17.8.

(C₂₀H₁₉O₅N)₂.H₂PtCl₆ requires Pt=17.6 per cent.

The *mercurichloride* and *aurichloride* are insoluble substances, having exactly the same appearance as the corresponding salts from narcotine.

The lactonic nature of the substance is proved by the following experiment. The base was dissolved in alcoholic potassium hydroxide, and was not precipitated by dilution with water. The solution contains the potassium salt of a hydroxy-acid analogous to the narcotates. On acidifying the liquid with hydrochloric acid, a colourless solution was obtained, from which ammonia precipitates the regenerated alkaloid. The substance melted after crystallisation from methyl alcohol at 198°, and its melting point was not lowered by admixture with a specimen of the substance which melted at 200°.

Anhydrocotarninephthalide Picrate.:—This derivative has been used to prove the identity of the base obtained in (a), (b), and (c).

When a solution of the base in dilute hydrochloric acid is treated with aqueous picric acid, a yellow precipitate of the picrate is obtained. The substance may be crystallised from acetone, and forms intense yellow prisms, melting at 202—203° [methods (a) or (b)], 200° [method (c)], 201° [mixed (b) and (c)].

A pure specimen of anhydrocotarninephthalide may be easily converted into picrate by mixing its hot alcoholic solution with alcoholic picric acid, when the salt crystallises out, and shows the correct melting point:

0.1290 gave 0.2549 CO₂ and 0.0491 H₂O. C=53.7; H=4.2.

C₂₆H₂₂O₁₂N₄ requires C=53.6; H=3.7 per cent.

The mother liquors, from the crystallisation of the hydrochloride in (b), gave a picrate undoubtedly quite different to the one just described. It is more sparingly soluble, and crystallises from acetone in tiny octahedra, melting at 240—241°:

0.1091 gave 0.2171 CO₂ and 0.0419 H₂O. C=54.2; H=4.2.

C₂₆H₂₂O₁₂N₄ requires C=53.6; H=3.7 per cent.

This new picrate is therefore isomeric with the picrate of anhydrocotarninephthalide. We do not think, however, that it is derived from a β-anhydrocotarninephthalide, but rather from a substance of the type of nornarceine.

The quantity of the substance available for investigation was so small that we were forced to abandon our inquiry.

Oxidation of Anhydrocotarninephthalide.

This oxidation was accomplished under the same conditions as were used for narcotine (Anderson, *Annalen*, 1853, 86, 187).

Anhydrocotarninephthalide (2 grams) was dissolved in water (10 c.c.) and nitric acid (4 c.c., D 1.42) by warming to 50° on the water-bath. The solution was then maintained at this temperature for three hours, and then allowed to remain until cold. During the course of the oxidation, gas, but no nitrous fumes, was evolved, and a pale yellow solution resulted. The acid liquid was saturated with sodium chloride, and repeatedly extracted with ether. The combined ethereal solutions were washed with water, and dried with sodium sulphate. On evaporation, a syrup was left, which was very soluble in water, and could not at first be brought to crystallisation. Ultimately, however, crystals were obtained, and these, on recrystallisation from water, were found to consist of phthalaldehydic acid, since, after careful drying, they melted at 96°.

and yielded phthalimide (m. p. 230°) on boiling with hydroxylamine hydrochloride in alcoholic solution.

The aqueous liquid, from which the acid was extracted, yielded on treatment with aqueous picric acid, a yellow precipitate, which was collected, and crystallised from hot water and then again from alcohol. It was obtained in silky, yellow needles, melting at $139\text{--}143^{\circ}$, and was obviously identical with the characteristic picrate of cotarnine (compare Salway, *loc. cit.*).

Phthalaldehydic acid and cotarnine are also the products when the base is oxidised with manganese dioxide and dilute sulphuric acid. The acid was recognised by its colour reactions with concentrated sulphuric acid and impure benzene and xylene, whilst the picrate of cotarnine was obtained from the filtered solution after the oxidation.

Dedimethoxynarceine (Formula V, p. 1155).

Anhydrocotarninephthalide was boiled for half an hour with an excess of methyl iodide. The base dissolved at first to a clear solution, but very quickly crystals of the methiodide separated. The unchanged methyl iodide was removed by distillation, leaving a pale yellow, crystalline residue. The compound crystallises from methyl alcohol in colourless prisms, melting and decomposing at 207° . It is sparingly soluble in cold water, methyl or ethyl alcohols. When heated in aqueous solution with precipitated silver chloride, silver iodide and the methochloride are produced.

The filtered solution was cooled, and rendered alkaline by the addition of a small excess of sodium hydroxide, when the milky solution first produced gradually resolved itself into a suspension of an amorphous precipitate of anhydrocotarninephthalide methyl hydroxide. This colourless ammonium base was collected, washed with water until free from alkali, and then boiled with a large excess of water for ten minutes. All but a small quantity of the substance passed into solution, which was filtered and concentrated to a small bulk. On allowing to remain in the cold, leaflets of *dedimethoxynarceine* separated in considerable quantity from the solution.

The substance was easily purified by crystallisation from water, in which it is quite soluble when hot, and sparingly so in the cold:

0.1477 gave 0.3520 CO_2 and 0.0832 H_2O . $\text{C}=65.0$; $\text{H}=6.2$.

$\text{C}_{21}\text{H}_{23}\text{O}_6\text{N}$ requires $\text{C}=65.4$; $\text{H}=6.0$ per cent.

Dedimethoxynarceine crystallises in colourless, lustrous laminæ, which, unlike narceine, are anhydrous; it melts at $189\text{--}190^{\circ}$. In all its reactions it shows great analogy to narceine, as the following description will prove.

The acidic character of the substance causes it to be soluble in alkaline carbonates, although it may be precipitated from the solution so formed by passing a very rapid stream of carbon dioxide. A concentrated solution in sodium carbonate, or in sodium hydroxide, deposits the sparingly soluble sodium salt as glistening plates. A cherry-red colour is developed on warming a small quantity of the substance with 50 per cent. sulphuric acid on the steam-bath.

Iodine acts on a suspension of the substance in water, producing a peculiar milky, brown liquid, which appears red to transmitted light, and on keeping, a deep brown precipitate separates. Dedi-methoxynarceine dissolves in chlorine water to a yellow solution, which on the addition of ammonia turns red, the colour being brighter than that obtained with narceine itself. Most of the salts of the base are readily soluble in water, but the *hydrochloride* separates from solutions that are not too dilute. It occurs, when crystallised fairly quickly, in microscopic bunches of needles, and melts and evolves gas at 172—174°:

The *platinichloride* is obtained in pale yellow needles when a solution of the hydrochloride in hot water is treated with platinum chloride:

0.1319 gave 0.0223 Pt. $Pt=16.9$,

$(C_{21}H_{23}O_6N)_2 \cdot H_2PtCl_6$ requires $Pt=16.6$ per cent.

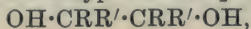
In conclusion, we desire to state that much of the expense connected with this investigation has been met by grants from the Research Funds of the Royal Society and of the Chemical Society.

THE UNIVERSITY,
MANCHESTER.

CXXIV.—*Synthesis of Pinacones. Part I.*

By WILLIAM PARRY.

OF the two classes of pinacones, symmetrical and unsymmetrical, the former, which are of the type $OH \cdot CR_2 \cdot CR_2 \cdot OH$ or



are, as is well known, produced along with secondary alcohols by reduction of ketones, generally with sodium or sodium amalgam.

In the case of aromatic ketones, such as acetophenone and benzophenone, it has been shown that mere exposure of their solution in alcohol to direct sunlight for many days is sufficient to effect the reduction, aldehydes being produced simultaneously (Ciamician and

Silber, *Ber.*, 1900, **33**, 2912). In 1904 S. F. Acree (*Ber.*, **37**, 2754) pointed out that symmetrical pinacones are easily obtained by the action of magnesium alkyl or aryl bromides on diketones, such as benzil; and he stated that unsymmetrical pinacones, which are of the type $\text{OH}\cdot\text{CR}_2\cdot\text{CR}'_2\cdot\text{OH}$ or $\text{OH}\cdot\text{CR}_2\cdot\text{CR}'/\text{R}''\cdot\text{OH}$, should be obtainable by the action of these reagents on the chlorides or esters of disubstituted glycollic acids. He succeeded in preparing benzo-pinacone in good yield, both from benzil and from methyl benzilate.

The author, after communication with Dr. Acree, and with Professor Percy F. Frankland, who had reserved the study of the action of Grignard's reagents on the esters of hydroxy-acids (*Trans.*, 1904, **85**, 1666), has examined the action of these reagents on ethyl α -hydroxyisobutyrate, which had been prepared by a method already explained (*Proc.*, 1909, **25**, 290).

The ester reacts normally with production of unsymmetrical pinacones, a few of which are now described.

EXPERIMENTAL.

Pinacone Hydrate, $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{OH}$, $6\text{H}_2\text{O}$.

The product of the interaction of ethyl α -hydroxyisobutyrate (22 grams) dissolved in three volumes of dry ether and ethereal magnesium methyl iodide (12 grams Mg) was decomposed by pouring gradually into a concentrated ice-cold solution of ammonium chloride. After evaporation of the ether, the residue distilled up to 165° as a colourless oil, which was boiled with water, and the solution concentrated under diminished pressure to a small volume.

Transparent plates (0.72 gram) separated, which melted at $44\text{--}47^\circ$, and a mixture of this substance and pinacone hydrate melted within the same limits. A further amount, corresponding with 3.5 grams, was found to be contained in the saline solution after separation of the ether, and was recovered by distilling the latter in a current of steam and evaporating almost to dryness in a vacuum desiccator over sulphuric acid.

β -Methyl- γ -ethylpentane- $\beta\gamma$ -diol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CEt}_2\cdot\text{OH}$, and *Diethylisopropenylcarbinol*, $\text{CH}_2\cdot\text{CMe}\cdot\text{CEt}_2\cdot\text{OH}$.

To an ethereal solution of magnesium ethyl bromide (12 grams Mg), 22 grams of ethyl α -hydroxyisobutyrate dissolved in dry ether were gradually added, and the mixture left for two days without heating.

After decomposition in the usual manner and removal of the ether, the residual liquid, which had a blue tint, was distilled

under 20 mm. pressure, when 13 grams of a colourless oil were obtained, boiling constantly at 100° :

0.1302 gave 0.3139 CO_2 and 0.1466 H_2O . $\text{C}=65.75$; $\text{H}=12.51$.

$\text{C}_8\text{H}_{18}\text{O}_2$ requires $\text{C}=65.69$; $\text{H}=12.4$ per cent.

β -Methyl- γ -ethylpentane- $\beta\gamma$ -diol is a viscid oil, which does not crystallise even when cooled to -15° . It dissolves in boiling water, but, on evaporation at the ordinary temperature in a desiccator, no separation of a crystalline hydrate takes place.

When distilled under the atmospheric pressure, water is eliminated, and the thermometer rises gradually to a maximum of 205° . After several such distillations, a fairly large quantity can be collected between 140° and 160° , and by systematic fractionation of this liquid a small amount of an oil is eventually obtained, which boils at 150 — $152^{\circ}/767$ mm., and has, especially when warm, a powerful odour of camphor.

It is unsaturated, since its solution in chloroform at once decolorises bromine dissolved in the same solvent. (Found, $\text{C}=74.39$; $\text{H}=12.88$. Calc., $\text{C}=75$; $\text{H}=12.5$ per cent.) This oil is evidently diethylisopropenylcarbinol, which has already been described by Courtot (*Bull. Soc. chim.*, 1906, [iii], **35**, 969) as the sole product of the action of magnesium ethyl iodide on ethyl α -methylacrylate.

β -Methyl- γ -propylhexane- $\beta\gamma$ -diol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CPr}_2^{\alpha}\cdot\text{OH}$.

Ethereal solutions of magnesium propyl bromide (12 grams Mg) and ethyl α -hydroxyisobutyrate (20 grams) were mixed, and, after warming for half an hour, left for three days at the ordinary temperature.

After the usual procedure, the reaction product was a blue liquid, which was distilled under 15 mm. pressure. The main quantity passed over at 105 — 108° (mostly at 105°) as a viscid oil (12 grams):

0.1323 gave 0.3332 CO_2 and 0.1551 H_2O . $\text{C}=68.69$; $\text{H}=13$.

$\text{C}_{10}\text{H}_{22}\text{O}_2$ requires $\text{C}=68.9$; $\text{H}=12.73$ per cent.

β -Methyl- γ -propylhexane- $\beta\gamma$ -diol is a colourless, viscid oil, which does not solidify when cooled in a freezing mixture. It boils at $105^{\circ}/15$ mm. When distilled under the ordinary pressure, it loses the elements of water, and yields an unsaturated liquid, which was not, however, obtained pure enough for identification.

$\alpha\alpha$ -Diphenyl- β -methylpropane- $\alpha\beta$ -diol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CPh}_2\cdot\text{OH}$.

This was prepared from magnesium phenyl bromide (18 grams Mg) and ethyl α -hydroxyisobutyrate (30 grams). The mixture was heated on the water-bath for six hours, and left overnight.

After decomposition with dilute sulphuric acid and removal of the ether, the red oil which was left was distilled in a current of steam to separate bromobenzene and diphenyl. The residue in the flask solidified, on cooling, to a yellow cake (47 grams), which was crystallised, first from a mixture of benzene and light petroleum, and then twice from aqueous alcohol (25 grams):

0.1997 gave 0.5768 CO_2 and 0.1310 H_2O . $\text{C}=78.78$; $\text{H}=7.34$.

0.1705, in 22.25 benzene, gave $\Delta t - 0.157^\circ$. $\text{M.W.}=243$.

0.4510 ,, 22.25 ,, ,, $\Delta t - 0.4^\circ$. $\text{M.W.}=253$.

$\text{C}_{16}\text{H}_{18}\text{O}_2$ requires $\text{C}=79.33$; $\text{H}=7.43$ per cent. $\text{M.W.}=242$.

αα-Diphenyl-β-methylpropane-αβ-diol crystallises from dilute alcohol in rosettes of white, silky needles, which melt at $89-89.5^\circ$. Its symmetrical isomeride, from acetophenone, melts at 122° . It is very soluble in all the common organic media, with the exception of light petroleum, in which it is almost insoluble.

When the pinacone (5 grams) was mixed with acetic anhydride (20 grams) and two drops of sulphuric acid added, solution took place at once, with evolution of heat. After remaining for a week at the ordinary temperature, the yellow liquid was poured into water, the solid collected, washed, and dried in a vacuum over sulphuric acid.

It was crystallised twice from aqueous alcohol, and analysed:

0.1491 gave 0.4671 CO_2 and 0.1031 H_2O . $\text{C}=85.44$; $\text{H}=7.68$.

$\text{C}_{16}\text{H}_{16}\text{O}$ requires $\text{C}=85.66$; $\text{H}=7.2$ per cent.

The substance is therefore a dehydration product of the pinacone, and is probably *α-diphenyldimethylethylene oxide*, $\begin{matrix} \text{CMe}_2 \\ | \\ \text{CPH}_2 \end{matrix} > \text{O}$.

It separates from dilute alcohol or from light petroleum in colourless prisms, which melt at $44-45^\circ$.

Its molecular weight was determined by the cryoscopic method:

Grams of substance per 100 grams of benzene.	Δt .	Molecular weight.
0.849	-0.233°	182
1.6	0.421	189
2.384	0.579	206
4.561	1.067	214
6.382	1.493	214

$\text{C}_{16}\text{H}_{16}\text{O}$ requires $\text{M.W.}=224$.

On allowing the benzene solution, which was originally colourless, to evaporate spontaneously, it acquired a yellow tint, and, after all the solvent had disappeared, the substance separated in transparent prisms, mixed with a small amount of a yellow oil, and at the same time there was a pronounced odour of acetophenone. No explanation has been found of this curious behaviour, but experiments are being conducted with larger quantities of material.

αα-Dibenzyl-β-methylpropane-αβ-diol, $\text{OH} \cdot \text{CMe}_2 \cdot \text{C}(\text{CH}_2\text{Ph})_2 \cdot \text{OH}$,
and *Dibenzylisopropenylcarbinol*, $\text{CH}_2 \cdot \text{CMe} \cdot \text{C}(\text{CH}_2\text{Ph})_2 \cdot \text{OH}$.

A solution of 26 grams of ethyl α -hydroxyisobutyrate in 50 c.c. of dry ether was poured gradually into magnesium benzyl chloride (16 grams Mg) dissolved in 250 c.c. of ether. The mixture was warmed on the water-bath for one hour and left overnight.

After decomposition, the ether was distilled without drying, and through the yellow oil thus obtained, steam was blown for three hours to separate dibenzyl, which had been formed in quantity. The residue in the flask did not solidify on cooling. It was dissolved in ether, the solution dried, and the ether expelled. The residual red oil was placed in a vacuum desiccator, where, after a few days, it partly solidified. It was filtered, the solid pressed out on a porous plate, and, when dry, crystallised from light petroleum (5 grams):

0.1778 gave 0.5190 CO_2 and 0.1322 H_2O . $\text{C} = 79.61$; $\text{H} = 8.26$.

0.4603, in 16.00 benzene, gave $\Delta t = 0.571^\circ$. M.W. = 252.

0.9206, „ 16.00 „ „ $\Delta t = 1.046^\circ$. M.W. = 275.

$\text{C}_{18}\text{H}_{22}\text{O}_2$ requires $\text{C} = 79.95$; $\text{H} = 8.2$ per cent. M.W. = 270.

αα-Dibenzyl-β-methylpropane-αβ-diol is readily soluble in all the common organic solvents, and crystallises from slightly dilute alcohol or from light petroleum in colourless prisms, which melt at $47\text{--}48^\circ$.

The red oil from which the solid pinacone had been filtered was distilled under 12 mm. pressure, when a small quantity of a yellow oil passed over between $165\text{--}168^\circ$. It was unsaturated, instantly decolorising a solution of bromine in chloroform:

0.2200 gave 0.6960 CO_2 and 0.1718 H_2O . $\text{C} = 86.28$; $\text{H} = 8.68$.

$\text{C}_{18}\text{H}_{20}\text{O}$ requires $\text{C} = 85.66$; $\text{H} = 8.00$ per cent.

These numbers, together with its unsaturated nature, indicate that the substance is impure *dibenzylisopropenylcarbinol*, $\text{CH}_2 \cdot \text{CMe} \cdot \text{C}(\text{CH}_2\text{Ph})_2 \cdot \text{OH}$, but the quantity obtained did not admit of further rectification.

αα-Dinaphthyl-β-methylpropane-αβ-diol, $\text{OH} \cdot \text{CMe}_2 \cdot \text{C}(\text{C}_{10}\text{H}_7)_2 \cdot \text{OH}$.

For the preparation of this substance, ethyl α -hydroxyisobutyrate (15 grams), dissolved in ether (30 c.c.), was added to an ethereal solution of magnesium α -naphthyl bromide (6 grams Mg), and the mixture was heated on the water-bath for six hours. After decomposition and removal of the ether, the product was a red liquid with a faint green fluorescence. It was distilled in a current of steam to separate the naphthalene, and the brown, viscid oil which

was left in the flask solidified, on cooling, to a brown cake. This was dissolved in a mixture of benzene and light petroleum, and, on long keeping, a small quantity of an almost colourless solid was eventually isolated, which was crystallised twice from alcohol (1·5 grams):

0·1137 gave 0·3487 CO_2 and 0·0668 H_2O . $\text{C}=83·64$; $\text{H}=6·53$.

0·4642, in 19·8 benzene, gave $\Delta t = 0·35^\circ$. $\text{M.W.}=335$.

$\text{C}_{24}\text{H}_{22}\text{O}_2$ requires $\text{C}=84·17$; $\text{H}=6·48$ per cent. $\text{M.W.}=342$.

αα-Dinaphthyl-β-methylpropane-αβ-diol separates from alcohol in small, white crystals, melting at $166\text{--}166·5^\circ$. It is not so soluble in the usual organic solvents as the phenyl and benzyl compounds.

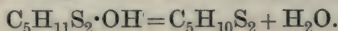
The author takes this opportunity of acknowledging his indebtedness to Dr. Alexander Rule, of the University of Liverpool, for much kind assistance with the analyses, and to the Research Fund Committee of the Chemical Society for a grant from which the cost of the materials used in this investigation has, in part, been met.

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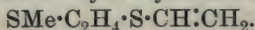
CXXV.—*The Decomposition of Diethylenesulphide-methylsulphine Hydroxide in Aqueous Solution.*

By LEILA GREEN and BRENDA SUTHERLAND.

DIETHYLENE disulphide was shown by Masson (Trans., 1886, **49**, 233) to unite with methyl iodide to form the salt diethylenesulphide-methylsulphine iodide, $\text{S} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{S} < \begin{smallmatrix} \text{I} \\ \text{Me} \end{smallmatrix}$. From this he prepared several other salts of the same base, and he showed that the base itself, obtained in aqueous solution by shaking the iodide with silver oxide and water, is strongly alkaline, but undergoes slow conversion into a neutral oil. Mansfeld (Ber., 1886, **19**, 696, 2658) obtained this oil in a pure state, and showed that it results from a spontaneous dehydration of the hydroxide:

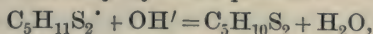


V. Meyer (Ber., 1886, **19**, 3262) gave reasons in support of the theory that this oil is the methyl vinyl ether of thioglycol,



The above formulation of the action makes it appear uni-

molecular; and in 1886 there was no reason to anticipate anything else; but, in the light of the ionic theory, it seems probable that it is expressed more correctly by the equation:



making it an ionic action of the second order. If so, the case is somewhat analogous to that of the conversion of ammonium cyanate into carbamide, which Walker and Hambley (Trans., 1895, 67, 746) proved to be a bimolecular reaction between the NH_4' and CNO' ions, and not the unimolecular transformation that had been tacitly assumed. It has, indeed, been objected that in such cases the bimolecular action of the ions cannot be distinguished from a unimolecular action of the non-ionised fraction of the substance; but this objection applies only in cases where Ostwald's dilution law holds good, that is, where C_i^2 varies as C_s , and it is very far from applicable to the case of any strong electrolyte, such as ammonium cyanate or the alkaline sulphine base. In such cases it seems fair to assume that the action, if ionic, will prove in dilute solution to be bimolecular with respect to the total solute (since the ionisation is nearly complete), and that it will vary in velocity directly as the total concentration of each ion, if either be increased by the addition of a suitable compound; whereas it should not show such simple relations to the total concentrations if it depended merely on the spontaneous change of the non-ionised fraction.

At Professor Masson's suggestion we have carried out an investigation of the decomposition of the sulphine base, and we have obtained results which seem to show conclusively that the action is of the second order, and ionic.

EXPERIMENTAL.

In order to obtain the solution of sulphine hydroxide, aqueous solutions of the sulphine iodide (0.1—0.2*N*) were decomposed by shaking with excess of moist silver oxide, and filtered from the resulting silver iodide and excess of oxide. The base was also prepared in two cases by interaction between lead hydroxide and the iodide, or barium hydroxide and the sulphate (formed from the iodide by the action of silver sulphate).

The hydroxide solution was titrated against approximately *N*/20-hydrochloric acid, using methyl-orange as indicator. A measured volume of the hydroxide (5 or 10 c.c.) was placed in each of a set of test tubes, which were then closed with corks provided with a tube drawn out to a capillary to allow of expansion of air on heating. The tubes were simultaneously immersed in a water-bath at 55°, this having been found by previous experiment to be

a temperature at which the decomposition can be conveniently followed. The utmost range of temperature was 0.1° in any one experiment, and 0.3° in the whole series.

At intervals the test tubes were removed, and cooled under running water, and the contents were then titrated under the same conditions as the original solution, the decrease of alkalinity giving the amount of decomposition.

The results of eight experiments with pure aqueous solutions of the base are summarised in table I. In the first column is given the number of the experiment; in the second, the initial concentration (A); in the third, the range of action or percentage decomposition observed; in the fourth, fifth, and sixth, the minimum, maximum, and mean values of K , calculated by the bimolecular equation:

$$K = \frac{1}{t} \frac{x}{A(A-x)},$$

where x is the amount decomposed in time t .

The units employed are the minute and the gram-molecule per litre.

Sample 6 was prepared from the sulphine sulphate and barium hydroxide, sample 4 from the iodide and lead hydroxide; the rest were made in the ordinary way from the sulphine iodide and silver oxide.

TABLE I.

No.	A .	Range.	K .		
			Minimum.	Maximum.	Mean.
1	0.0474	75	0.101	0.119	0.115
2	0.0637	67	0.086	0.095	0.092
3	0.0667	70	0.097	0.102	0.100
4	0.0734	70	0.099	0.110	0.103
5	0.0744	76	0.097	0.107	0.103
6	0.0805	70	0.096	0.101	0.099
7	0.1274	75	0.082	0.088	0.085
8	0.1475	75	0.085	0.090	0.088

It may be pointed out that this method of summarising the results, by emphasising those which deviate most from the mean, rather disguises the actual regularities. Inspection of the complete figures leaves no doubt that the errors in each experiment are irregularly distributed, and that the bimolecular formula is correct. The unimolecular formula entirely fails. Comparison of the different experiments suggests that the value of K is, to some extent, dependent on that of A , being smaller in stronger solutions; but there is no certain indication of a corresponding increase of K during the progress of any single experiment, such as would point to the influence of increasing ionisation.

Influence of Added Ions.—If either sodium hydroxide or the sulphine iodide be added beforehand to the sulphine hydroxide solution, the ionic concentrations are unequal, and (on the usual simplifying assumption of total ionisation) the integrated bimolecular equation is:

$$K = \frac{1}{t}(B - A)\log_e \frac{A(B - x)}{B(A - x)},$$

where A = initial total concentration of $(OH)'$.

B = initial total concentration of $(C_5H_{11}S_2)'$.

x = amount of sulphine base decomposed in time t .

In experiments 9 and 10 the sulphine hydroxide solution contained a known amount of the iodide, thus making B greater than A ; whilst in experiments 11 and 12 it contained a known amount of sodium hydroxide, so that A was greater than B . Results of the four tests are summarised in table II. In the first column is the number of the experiment; in the second and third the values of A and B respectively; in the fourth, the range of action; in the fifth, sixth, and seventh, the minimum, maximum, and mean values of K .

TABLE II.

No.	A .	B .	Range.	K .		
				Minimum.	Maximum.	Mean.
9	0·0570	0·1270	80	0·073	0·094	0·084
10	0·0818	0·1218	80	0·080	0·090	0·087
11	0·1334	0·0570	93	0·083	0·087	0·085
12	0·1254	0·0818	88	0·085	0·092	0·088

The values obtained for K are in these cases very similar to those of experiments 7 and 8 of table I, and it may be pointed out that in all of these tests the initial total ionic concentration is, very approximately, the same, namely, between 0·12 and 0·15.

Summary of Results.

(1) The spontaneous decomposition of diethylenesulphidemethylsulphine hydroxide in dilute aqueous solution, which is a process of dehydration, and results in the formation of the neutral oil $C_5H_{10}S_2$, is a reaction of the second order with respect to the sulphine base.

(2) Experiments with solutions of the sulphine base containing excess of either of its ions (added sodium hydroxide or sulphine iodide) give results in accordance with the theory that the action occurs between these ions, its velocity being proportional to the concentration of each.

(3) The bimolecular constant diminishes somewhat with increase of the initial total ionic concentration, and the effects are much the same, whether due to added sodium hydroxide, sulphine iodide, or simply to increase of the sulphine hydroxide itself.

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CXXVI.—*Purification of Acetic Acid.*

By KENNEDY JOSEPH PREVITÉ ORTON, MURIEL GWENDOLEN EDWARDS, and HAROLD KING.

ALTHOUGH the ordinary commercial acetic acid * (melting at about 16°) is attacked by chlorine and bromine, we find that the highly purified acid is not, if light is excluded. The reaction of these impurities in the commercial acid with chlorine and bromine is greatly accelerated on dilution with water.

In the investigation of the chlorination and bromination of anilines, anilides, etc. (Orton and Jones, *Trans.*, 1909, **95**, 1456; *Proc.*, 1909, **25**, 233, 305; *Brit. Assoc. Reports*, 1910), and in the determining of the solubility coefficients of chlorine and bromine in various dilutions of acetic acid (Jones, this vol., p. 392), it became necessary to obtain acetic acid which did not affect the reagents. It was not sufficient to allow chlorine or bromine to be added to the acetic acid until the impurities were removed, as the hydrogen chloride or bromide then formed interfere with the measurements which were to be made.

The purity of the acetic acid in this respect can be very easily determined by following the fall of titre of a solution of bromine in the acetic acid diluted with an equal volume of water. The solution must, of course, be thoroughly shielded from light. The typical behaviour of an ordinary good commercial acetic acid is shown in the following experiment, which illustrates the method employed.

A standard solution of bromine of about $N/5$ is made up in pure acetic acid. Five c.c. of this solution are added to 45 c.c. of the acetic acid to be tested, and 50 c.c. of water are introduced. The mixture is placed in a bath at 16° , and the free bromine estimated at intervals with hydriodic acid and $N/50$ -thiosulphate.

* Kahlbaum's "K" acetic acid, which has recently appeared in the catalogue, does not react appreciably with chlorine or bromine in the dark.

Interval in minutes.	Volume of mixture withdrawn.	Titre in c.c. of <i>N</i> /50-thiosulphate.
0	10	5.02
15	10	2.64
90	10	0.73
180	10	0.245

With a pure acetic acid the following results were obtained :

0	10	5.02
15	10	4.96
90	10	4.94
180	10	4.95

The use of potassium permanganate in place of bromine is not to be recommended. Permanganate is reduced by the impurities, but the reaction is not so rapid, and the test is less sharp and definite.

A relation exists between the Adamkiewicz protein reaction and the purity of acetic acid as estimated by the absorption of bromine; an acid which gives the former reaction, obviously reduces bromine readily.

Experiment has shown that the removal of the impurities by fractional freezing or fractional distillation can only be effected with very great loss. In the distillation, no completely pure acid was obtained; the impurities pass over slowly, leaving a purer acid in the distilling flask. By freezing, only some 10—15 per cent. of the acid was finally obtained entirely freed from impurity.

The following table shows the results of fractionally distilling a specimen of impure glacial acetic acid melting at 16.31°. Under "bromine absorbed" the number of c.c. of *N*/50-bromine is given which disappears in one hour when the acetic acid is treated as described in the foregoing.

Fraction (100 c.c.).	Boiling point.	Melting point.	"Bromine absorbed."
<i>A.</i>	115—115.7°	15.81°	3.34 c.c.
<i>B.</i>	115.7	16.41	1.83 "
<i>C.</i>	115.7	16.41	
<i>D.</i>	115.6	16.41	1.53 "
<i>E.</i>	115.6—115.5	16.51	
<i>F.</i>	115.5	16.51	1.00 "

The following table shows the results of partial freezing of a specimen of acetic acid which melted at 16.4°:

Separation.	Melting points of		"Bromine absorption" of liquid drawn off.
	(i) Residue.	(ii) Liquid drawn off.	
1	16.49	16.13	2.42
2	16.5	16.31	2.05
3	16.51	16.31	1.89
4	16.51	16.36	0.90

The final residue, melting at 16.51°, showed bromine absorption equal to 0.087 c.c. *N*/50-bromine. The low melting of the later

fractions of the "liquid drawn off" is probably due to water introduced before the melting point was taken.

It is noteworthy that the melting point of the acetic acid is identical with those observed by Squire and Caines (*Pharm. J.*, 1902, [iv], **15**, 413) and by Jones and Murray (*Amer. Chem. J.*, 1904, **30**, 193). We learn from Mr. W. R. Bousfield and Dr. Lowry that they prepared a pure acetic acid some years ago; we have tested a specimen of their acid prepared in 1902, and found it stable to bromine and incapable of giving the Adamkiewicz reaction. The following are some of the melting points which have been recorded for acetic acid: 16.75° (Rudorff, *Ber.*, 1870, **3**, 390); 16.55° (Peterson, *J. pr. Chem.*, 1881, [ii], **24**, 296); 17.5° (Sonstadt, *Jahresber.*, 1878, 34); 16.4° (Ramsay and Young, *Trans.*, 1886, **49**, 805; 16.6713° (de Visser, *Rec. trav. chim.*, 1893, **12**, 115, 154); 16.5° (Squire and Caines, *loc. cit.*; Jones and Murray, *loc. cit.*)

Hopkins and Cole (*Proc. Roy. Soc.*, 1901, **68**, 21) showed conclusively that ordinary acetic acid contained glyoxylic acid (the cause of the Adamkiewicz reaction), probably together with traces of other impurities. Doubtless this acid is one of the substances which react with bromine.

Purification of Acetic Acid from Substances which React with Chlorine and Bromine.

We have found that ordinary glacial acetic acid can be easily freed with but little loss from the substances which react with chlorine or bromine, or which are necessary to the Adamkiewicz reaction, by distillation from phosphoric oxide. As is, of course, well known, treatment of fatty acids with phosphoric oxide leads to the formation of the acid anhydride. In the case of acetic acid, however, if the proportion of phosphoric oxide is correctly chosen, only traces of acetic anhydride are produced (compare Gall and Etard, *Ber.*, 1875, **9**, 444).*

In the purification, such a quantity of phosphoric oxide is used as will form orthophosphoric acid with the water in the acetic acid, but the correct quantity of phosphoric oxide depends somewhat on the quality of the acetic acid. We have not started with an acid melting below 16° . The water is estimated from the melting point. Usually about two litres are distilled in one opera-

* W. H. Perkin, sen. (*Trans.*, 1884, **45**, 481), when preparing acetic acid for the purpose of determining the magnetic rotation, states: "Ordinary glacial acetic acid was dried in two ways. One quantity was treated with phosphoric anhydride, and then distilled." Ramsay and Young (*loc. cit.*) express the opinion that small quantities of acetic anhydride are produced when acetic acid is dried in this way.

tion; the first 50 c.c. (although free from the materials which react with bromine) are collected separately, as the melting point may be a few tenths of a degree too low. About 1700 c.c. are then collected as a single fraction, and found to melt at $16\cdot4$ — $16\cdot5^{\circ}$.

The traces of acetic anhydride which are found in the distillate have been estimated in a number of samples of the purified acid by the method which is described in the following paper. The quantities varied from 0·009 gram to a maximum of 0·04 gram per 100 c.c. of the purified acid. Such traces are entirely without effect for the purposes for which the acid was used.

Deterioration of the purified acid on keeping has not been observed, even when no special precautions are taken to shield the acid from light or contact with dry air. This is remarkable, since Hopkins and Cole (*loc. cit.*) state that a specimen of acetic acid which had been deprived of the power of giving the Adamkiewicz reaction by purification, recovered it in course of time.

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CXXVII.—*The Detection and Estimation of Small Quantities of Acetic Anhydride in Acetic Acid.*

By MURIEL GWENDOLEN EDWARDS and KENNEDY JOSEPH
PREVITÉ ORTON.

No accurate method of estimating acetic anhydride in the presence of large excess of acetic acid appears to be known. Menshutkin and Wasilieff (*J. Russ. Phys. Chem. Soc.*, 1896, **21**, 190) describe a method for mixtures which do not contain more than 40 per cent. acetic acid; the anhydride is caused to react with excess of aniline, and the equivalent of acetic acid which is thereby produced is titrated with baryta.

Our method is by the use of anilines which react very rapidly with acetic anhydride, but do not form anilides with acetic acid at the ordinary temperature. Further, it is necessary that the basic properties of the aniline should permit of an accurate separation from the anilide. The anilide must also be readily and quantitatively converted into a stable chloroamine. The accurate estimation of the latter is extremely easy by reason of its quantitative reaction with hydriodic acid, and the titration of the free iodine with thiosulphate.

Of the many anilines the acetylation of which we have been engaged in investigating, 2:4-dichloroaniline is to be preferred for the estimation of small quantities of acetic anhydride. It is possible to detect with the aid of this aniline, 0.005 gram of anhydride in 100 grams (1 in 20,000 parts) of glacial acetic acid or of diluted acetic acid. Proportions over 0.1 per cent. can be accurately estimated in 80—100 per cent. acetic acid.

The procedure is as follows: 2 grams of 2:4-dichloroaniline (or some larger quantity, which is about three times that equivalent to the acetic anhydride) is added to 100 c.c. of the acetic acid containing acetic anhydride. The mixture is kept in a bath at 16° for a few hours, for example, overnight. The reaction is extremely rapid, being nearly complete in a few minutes, but obviously considerable time is required for the last traces of the anhydride to disappear. The mixture is diluted with water to 20 per cent. acetic acid, and the aniline (partly) and the anilide (wholly) extracted with chloroform. For each 100 c.c. of the diluted liquid, first 10, secondly 7 c.c., and lastly 5 c.c. of chloroform are used. The separation of the last fraction of chloroform requires a little care. It is best finally to wash the aqueous acetic acid twice with one c.c. of chloroform. The unchanged aniline is now withdrawn from the chloroform solution by shaking for a few minutes with 10 per cent. hydrochloric acid, 160—200 c.c. being used for each gram of aniline originally added. The chloroform is very carefully drawn off into a separating funnel, and the hydrochloric acid washed twice with 1 c.c. of chloroform as above directed.

The chloroform is now mixed with about an equal volume of glacial acetic acid, and dilute bleaching powder solution slowly added. The amount of bleaching powder should be three to five times that required to convert all the possible anilide into chloroamine. The volume of the bleaching powder solution should be equal to the volume of the glacial acetic acid, that is, the acetic acid is diluted to 50 per cent., a concentration at which it has been shown (Orton and Jones, *Trans.*, 1909, **95**, 1456) that the reversible reaction, $\text{Ar}\cdot\text{NHAc} + \text{Cl}_2 \rightleftharpoons \text{Ar}\cdot\text{NClAc} + \text{HCl}$, is nearly complete from left to right. If the concentration of the acetic acid is higher, increasing quantities of chlorine and anilide remain in the system. On the other hand, if the volume of the bleaching powder solution is larger, there is a tendency for anilide to collect in the chloroform layer, and hence more prolonged shaking is required to bring about a complete conversion into the chloroamine.

An *N*/20-bleaching powder solution is now added in sufficient quantity to dilute the aqueous acetic acid to 20 per cent. acetic acid. For example, if 30 c.c. of glacial acetic acid were added to

the chloroform solution of the anilide, then 30 c.c. of bleaching powder solution would be required in the first addition, and 90 c.c. of $N/20$ -bleaching powder solution for the second. It has been found that chloroform withdraws this chloroamine completely from 20 per cent. acetic acid.

Any marked development of red colour at this stage shows that the aniline has not been properly separated.

The chloroform is drawn off into 30—40 c.c. of $N/20$ -bleaching powder solution, with which it is shaken in order to free it from acetic acid. Finally, the chloroform is evaporated in a current of pure dust-free air at a temperature not exceeding 25° .

The residue, generally oily and of a yellow to orange colour, is dissolved in chloroform (5—10 c.c.), and treated with 5 per cent. potassium iodide and a little acetic acid; the iodine is titrated with $N/20$ -thiosulphate.

We have tried to dispense with the separation of the aniline from the anilide, and have treated the mixture with acetic acid and bleaching powder. But although it is possible with practice to make fairly accurate estimations of the anilide (and hence of anhydride), the end-point of the titration of the iodine is wanting in sharpness owing to a slow reaction of the substances produced from the aniline and bleaching powder with the hydriodic acid.

The method was tested in various ways; by passing known weights of chloroamine through the operations where chloroamine was present in the above series; more rigidly by analysing known mixtures of aniline and anilide; and by making up known mixtures of acetic anhydride in various concentrations of acetic acid.

TABLE I.

The following results show the accuracy with which the chloroamine and anilide can be estimated:

	1.	2.	3.
Chloroamine used	0.215	0.2234	0.187
found	0.2138	0.2240	0.1852
Anilide used	0.1994	0.2100	0.0966
found	0.2016	0.2090	0.0986
Aniline (<i>circa</i>)	0.2	0.5	1.0

TABLE II.

The results of experiments in which varying weights of acetic anhydride in glacial acetic acid were used.

Acetic anhydride.	Aniline.	Volume of mixture.	C.c. of N/20-thio-sulphate.	Acetic anhydride found.	Error.
1. 0·135	0·5 (<i>circa</i>)	50 c.c.	51·7	0·1318	- 0·0032
2. 0·2002	0·5	50 „	77·1	0·1960	0·0042
3. 0·1430	0·5	50 „	56·0	0·1428	0·0002
4. 0·1100	0·5	50 „	43·0	0·1097	0·0003
5. 0·0815	2·0	100 „	12·0	0·0300	0·0015
6. 0·0228	2·0	100 „	8·8	0·0220	0·0008

TABLE III.

The following numbers were obtained when the aniline was not extracted with hydrochloric acid:

1. 0·1351	0·2704	50 c.c.	50·85	0·1296	- 0·0055
2. 0·0743	0·1479	50 „	27·75	0·0707	0·0036

TABLE IV.

Diluted acetic acid was used as medium.

A.—Medium is 90 per cent. acetic acid.

1. 0·1474	0·5 (<i>circa</i>)	50 c.c.	57·00	0·1453	- 0·0025
2. 0·1400	0·5	50 „	55·00	0·1402	+ 0·0002

B.—Medium is 80 per cent. acetic acid.

1. 0·1478	1·0 (<i>circa</i>)	50 c.c.	57·85	0·1474	- 0·0004
2. 0·1104	1·0	50 „	42·4	0·1084	0·002

C.—Medium is 50 per cent. acetic acid.

1. 0·1431	1·0	50 c.c.	53·85	0·1372	- 0·0058
2. 0·1404	1·0	50 „	53·1	0·1354	0·0050

Obviously, in dilute acetic acids the aniline and the water are competing for the acetic anhydride. The numbers in table IV prove, when the relative concentrations of the aniline and water are taken into account, how vastly greater is the speed of the interaction of the aniline and anhydride. Only when the water is 50 per cent. of the medium does the hydrolysis of the anhydride become appreciable. That the speed of the acetylation of 2:4-dichloroaniline by acetic anhydride is very great, is further emphasised by the fact that acetic anhydride in solution in 80 per cent. acetic acid is completely hydrolysed in sixteen hours at the laboratory temperature. Yet (see table IV, *B*) acetic anhydride appears to react all but entirely with the aniline in that medium; the results of a large number of estimations of acetic anhydride in 80 per cent. acetic acid show an apparent loss of 3—4 per cent.

2:4-Dichloroaniline is not acetylated by glacial acetic acid at 16° at an appreciable rate. A solution of 0.5 gram in 50 c.c. of glacial acetic acid (m. p. 16.5°) was kept at 16° for 10.75 days. No anilide was detected by the method here described.

On the other hand, when a solution of 0.1850 gram of the aniline in 25 c.c. of glacial acetic acid was boiled for thirteen hours, 0.1843 gram was found to have been converted into anilide.

We are engaged by the aid of this method in investigating the hydrolysis of acetic anhydride and the acylation of various anilines, and in the study of the effect of catalysts on the process.

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CXXVIII.—*A Method of Chlorination. Chlorination of Anilines and Phenols.*

By KENNEDY JOSEPH PREVITÉ ORTON and HAROLD KING.

IT is obvious from the literature that many difficulties have been met with in preparing simple chloro-derivatives of many anilines and phenols. Records exist of relative few of such compounds. In the case of phenols these difficulties appear to have been partly overcome by the use of sulphuryl chloride (Peratoner and others, *Gazzetta*, 1898, **28**, i, 197), but this agent cannot be used with anilines.

Although aniline (anilide) itself and chloro- and nitro-anilines can be easily chlorinated, the presence of one methyl group in *p*-toluidine gives such opportunity for oxidation or other reactions that the yield of monochloro-derivative is very small. Chlorination by means of standard solutions of chlorine in hydrochloric acid (Reed and Orton, *Trans.*, 1907, **91**, 1543) was found in some cases to be a convenient agent, as the rate of chlorination and the extent of oxidation could be controlled by adjusting the concentration of the hydrochloric acid. Above a certain concentration, 24 per cent., no action at all took place. On dilution to 20 per cent. a slow chlorination started, and little oxidation, or, with bromoanilines, displacement of bromine, occurred until the acid had been considerably further diluted. This method is, however, useless for phenols, and is not effective in the case of many homologues or derivatives of aniline (xylydines, etc.).

The method which we have found very successful is based on

the equilibrium existing between chloroamines, hydrogen chloride, anilides, and chlorine, $\text{Ar}\cdot\text{NCl}\cdot\text{Ac} + \text{HCl} \rightleftharpoons \text{Ar}\cdot\text{NH}\cdot\text{Ac} + \text{Cl}_2$, which was discovered by Orton and Jones (Trans., 1909, **95**, 1456). Whilst in dilute acetic acid, 50 per cent. and under, the system was nearly entirely composed of the two substances on the left hand side of the equation, with increase in the concentration of the acetic acid, the amount of anilide and chlorine increased, until in glacial acetic acid, chloroamine and hydrochloric acid could not be detected. Hence, in glacial acetic acid, by using definite small quantities of hydrogen chloride, it is possible to obtain given low concentrations of chlorine. If some other compound is present in which substitution by chlorine can occur, the chlorine reacts, and is replaced by an equivalent of hydrogen chloride. The acid, in its turn, reacts with the chloroamine, yielding a molecular proportion of chlorine. Hence the concentration of chlorine in the system remains constant, until (near the end of the chlorination) the amount of chloroamine remaining falls below the amount of hydrogen chloride originally added. In this way the concentration of the chlorine with some of the more refractory substances was maintained at such low values as 0.0105 gram-molecules per litre (0.021*N*). By this very delicate treatment oxidation can be either entirely prevented or greatly reduced, and the whole operation can be effectively controlled.

In choosing the chloroamine to be used, it is necessary that the anilide from which the chloroamine is derived should not itself chlorinate (in the nucleus) at an appreciable rate under the conditions, and secondly, that the anilide should have such a solubility in diluted acetic acid that its separation from the chlorinated compound can be readily carried out. 2:4-Dichloroacetanilide and *p*-nitroacetanilide will generally meet both requirements; *p*-nitroacetanilide is very sparingly soluble in glacial acetic acid (0.8 gram in 100 c.c. of glacial acetic acid; 0.4 gram in 100 c.c. of 50 per cent. acetic acid). 2:4-Dichloroacetanilide (6.4 grams in 100 c.c. of glacial acetic acid; 0.8 gram in 100 c.c. of 50 per cent. acetic acid) can be used when the chlorinated compound is very sparingly soluble in glacial or slightly diluted acetic acid, or when it is relatively very soluble in highly diluted acetic acid. Both chloroamines can be very readily prepared for this purpose by following the procedure described by Reed and Orton (Trans., 1907, **91**, 1554).

As the chlorination is carried out in very dilute solution in glacial acetic acid, attention must be directed to preventing loss of chlorine by interaction with the medium. In the first place, the solution must be shielded from light, which greatly accelerates the action

of chlorine on acetic acid. Further, the acetic acid must be freed from those products which react rapidly with halogens. For this purpose the acid is distilled from phosphoric oxide, as described by Orton, Edwards, and King (this vol., p. 1180). Other media, such as chloroform and carbon tetrachloride, are not suitable owing to the insolubility of hydrogen chloride, and the separation of insoluble hydrochlorides of aniline and anilides. Acetic anhydride may be used with advantage in certain cases, when acetylation is not to be feared; the speed of chlorination is greater, and oxidation is still less obvious in the anhydride than in the acid.

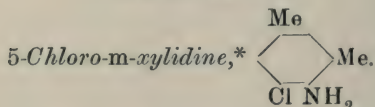
Usually the procedure adopted was to mix equivalent quantities of the compound to be chlorinated and the chloroamine in glacial acetic acid, and then to add 1/100th—1/20th gram-molecular proportion of hydrogen chloride in the form of the constant boiling aqueous solution (22 grams of HCl per 100 c.c.). The mixture was kept in the dark at 15°, and at properly chosen intervals 1 c.c. withdrawn, and the remaining chloroamine (and chlorine) estimated in order to determine when the reaction was complete. The time required varies widely from a few minutes to two to three days.

The method can be used in the case of all substances which chlorinate rapidly. It gives good results in the preparation of substances so sensitive to oxidation as *m*-xylidides, ψ -cumidides, *o*-anisidides, *o*- and *p*-phenetidides, and the cresols and *m*-xylenol. α -Naphthol, which is especially sensitive, serves as a test case, for it can be converted into a monochloro-derivative (or derivatives) without any concomitant oxidation. It is a far better way of preparing *s*-trichloroaniline from 2:4-dichloroaniline than by the usual method—the action of chlorine on a chloroform solution.

Further, it is an excellent method of introducing one chlorine atom into a given aniline or phenol which has more than one position capable of ready chlorination, for example, a para- or 3:4-disubstituted compound. Primarily, of course, the formation of a dichloro-derivative depends on the relative velocities of chlorination of the unsubstituted and the monochlorinated compounds. Probably without exception the unchlorinated compound has always a great advantage in speed of chlorination. But in the chlorination of anilines and anilides, the more basic, that is, the unchlorinated substance, preferentially combines with the hydrochloric acid produced, and hence is not attacked or more slowly attacked by the chlorine. In the method here described, owing to the reaction between hydrochloric acid and the chloroamine, there is no hydrogen chloride in the system until at least 19/20ths of the chlorination has taken place. Moreover, there is not, as in the passage of chlorine into a solution, any local excess of chlorine.

Hence, the condition for the production of a dichloro-derivative does not appear. As an illustration of its efficacy, it has been used in this laboratory to introduce chlorine atoms successively into *p*-hydroxydiphenylamine when all other methods failed.

EXPERIMENTAL.



Attempts to chlorinate *m*-xylidine in 20 per cent. hydrochloric acid solution or aceto-*m*-xylidide in glacial acetic acid gave no satisfactory result. The small quantities of monochloro-derivative which were produced could not be purified. Similarly, treatment of xylidine in acetic acid with chloroamine and hydrochloric acid was followed by considerable oxidation.

5-Chloroaceto-*m*-xylidide was prepared from aceto-*m*-xylidide in the following manner: A solution of 10 grams of the xylidide in 100 c.c. of glacial acetic acid was mixed with one equivalent of a chloroamine (14.62 grams of acetylchloroamino-2:4-chlorobenzene) in 400 c.c. of solvent, and 1/20th gram-molecular proportion (0.5 c.c.) of hydrochloric acid, as constant boiling aqueous solution, finally added. After keeping for seventy hours in the dark, only a trace of chlorine remained, which was removed by a few drops of sulphurous acid. The liquid was diluted to 50 per cent. acetic acid, and kept for three days, when the major quantity of the 2:4-dichloroacetanilide had separated. Further dilution caused separation of mixtures. Finally, the mother liquor, diluted to 5 per cent. acetic acid, was extracted with chloroform. Both the material separating from the lower dilutions of acetic acid and that obtained from the chloroform extract were recrystallised from alcohol, when the needles of the chloro-*m*-xylidide separated before the rhombs of the chloroanilide. Repeated crystallisation from alcohol gave finally the pure material. It crystallises in short prisms from alcohol or benzene, melting at 196.5—197.5°:

0.1887 gave 0.1365 AgCl. Cl=17.89.

$\text{C}_{10}\text{H}_{12}\text{ONCl}$ requires Cl=18.23 per cent.

5-Chloro-*m*-xylidine was prepared by boiling the xylidide with 10 per cent. aqueous hydrochloric acid until the solid had disappeared. The product was freed from colouring matter by

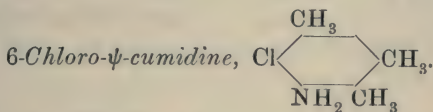
* Professor Auwers informs us that he was unable to obtain this compound by the chlorination of *m*-xylidine or aceto-*m*-xylidide, a dichloro-derivative being alone isolated.

distilling in a current of steam. It crystallises from dilute alcohol or petroleum in feathery needles, melting at 37—38°:

0.1901 gave 0.1755 AgCl. $\text{Cl} = 22.84$.

$\text{C}_8\text{H}_{10}\text{NCl}$ requires $\text{Cl} = 22.85$ per cent.

The position assigned to the chlorine is confirmed by the fact that the base in acetic acid solution does not react with bromine; all anilines in which an ortho- or the para-position with respect to the amino-group is unoccupied, react with bromine instantly.



Aceto- ψ -cumidine was treated in the manner just described. The chlorination was complete in forty-three hours. In this case, dilution of the acetic acid was followed by the separation of both 2:4-dichloroacetanilide and chloro- ψ -cumidine; hence, the use of the chloroamine of *p*-nitroacetanilide is to be preferred, as the nitroacetanilide mainly separates first. Crystallisation of the separations and the chloroform extract, first from alcohol, and subsequently from benzene, effected a complete separation.

6-Chloroaceto- ψ -cumidine crystallises in four-sided prisms from alcohol, and in needles from benzene, in which it is very sparingly soluble at the ordinary temperature. It melts at 208—209°:

0.1992 gave 0.1341 AgCl. $\text{Cl} = 16.65$.

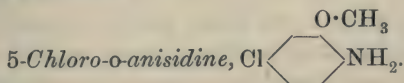
$\text{C}_{11}\text{H}_{14}\text{ONCl}$ requires $\text{Cl} = 16.75$ per cent.

6-Chloro- ψ -cumidine was prepared from the acetyl derivative by hydrolysing with boiling aqueous hydrochloric acid. It separates from dilute alcohol in long, slender needles, melting at 55—56°:

0.1828 gave 0.1529 AgCl. $\text{Cl} = 20.7$.

$\text{C}_9\text{H}_{12}\text{NCl}$ requires $\text{Cl} = 20.9$ per cent.

An attempt was made to prepare the corresponding 6-chloro- ψ -cumene by eliminating the amino-group in the usual way. An oil was isolated, in quantity, however, too small to be properly purified. It boiled at 213—215°, and on analysis gave $\text{Cl} = 21.75$, instead of 22.99 per cent.



The chlorination of aceto-*o*-aniside was more difficult, owing to the impossibility of avoiding oxidation. The method was similar to that described. The separation obtained on diluting the product of the reaction to 50 per cent. was mainly 2:4-dichloroacetanilide,

and that from 20 per cent. acetic acid was mainly the chloro-anisidide. It was purified by repeated recrystallisation from alcohol, in which it is very soluble. It forms six-sided plates melting at $142.5-143.5^\circ$:

0.2602 gave 0.1874 AgCl. $\text{Cl}=17.82$.

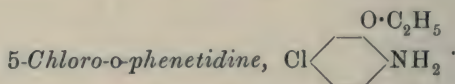
$\text{C}_9\text{H}_{10}\text{O}_2\text{NCl}$ requires $\text{Cl}=17.77$ per cent.

5-Chloro-o-anisidine was prepared by hydrolysing the acetyl derivative with 10 per cent. aqueous hydrochloric acid, and distilling the product in a current of steam after rendering alkaline. It crystallises from dilute alcohol in long, flattened needles, melting at $45-46^\circ$, and rapidly becomes discoloured in air:

0.1716 gave 0.1559 AgCl. $\text{Cl}=22.48$.

$\text{C}_7\text{H}_8\text{ONCl}$ requires $\text{Cl}=22.51$ per cent.

The constitution has been given as the most probable.



5-Chloroaceto-o-phenetidine was readily obtained from aceto-o-phenetidine. It separated mainly when the reaction mixture was diluted to 20 per cent., and was purified by repeated crystallisation from alcohol. It forms large, six-sided plates, melting at $105.5-106.5^\circ$:

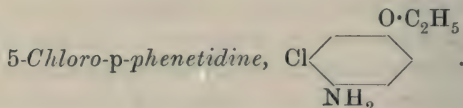
0.0594 gave 0.0389 AgCl. $\text{Cl}=16.20$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{NCl}$ requires $\text{Cl}=16.60$ per cent.

5-Chloro-o-phenetidine was obtained from the acetyl derivative and crystallised in long, flattened needles, melting at $21-22^\circ$:

0.1894 gave 0.1581 AgCl. $\text{Cl}=20.65$.

$\text{C}_8\text{H}_{10}\text{ONCl}$ requires $\text{Cl}=20.67$ per cent.



The procedure adopted in chlorinating aceto-p-phenetidine was the same as for the ortho-compound. The product from 20 per cent. acetic acid was crystallised from alcohol several times, and the pure 5-chloroaceto-p-phenetidine obtained in this way. It forms stellar groups of small needles from alcohol and benzene, melting at $128-129^\circ$:

0.1952 gave 0.1305 AgCl. $\text{Cl}=16.54$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{NCl}$ requires $\text{Cl}=16.60$ per cent.

The corresponding base, 5-chloro-p-phenetidine, was readily

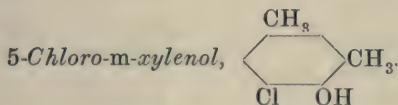
prepared and purified. It separates from dilute alcohol in plates or scales, melting at 64—65°. The *hydrochloride* crystallises in needles, but sparingly soluble in 10 per cent. hydrochloric acid:

0.2004 gave 0.1668 AgCl. Cl=20.60.

$C_8H_{10}ONCl$ requires Cl=20.67 per cent.

Chlorination of Phenols.

This method is particularly well adapted to the chlorination of phenols and naphthols. The reaction is extremely rapid, and the temperature may rise if the solutions are not very dilute. Oxidation is negligible. The separation of the chlorinated phenol from the anilide is obviously an easier matter than the separation of two anilides.



This compound appears to have been prepared (Falcke, *Diss.*, Marburg, 1906); it is mentioned as a product of the action of hydrogen chloride on 2:4-*m*-xylo- ψ -quinol by Bamberger (*Ber.*, 1907, **40**, 1904, 2268; Reber, *Diss.*, Zürich, 1903); but a description is not to be found in the literature which is ordinarily accessible.

Two grams of *m*-xylenol and the equivalent quantity of a chloroamine are mixed in 100 c.c. of glacial acetic acid, and 1/20th gram-molecular proportion of hydrochloric acid added. The chloroamine rapidly disappeared. Water was added, and the anilide collected. The phenol was extracted from the mother liquor reduced to 15 per cent. acetic acid by chloroform. The residue from the chloroform was dissolved in 100 c.c. of air-free 2 per cent. sodium hydroxide. After filtration, the phenol was set free by acid, and extracted by chloroform. After drying and evaporation, the phenol was obtained as a colourless, limpid oil of the usual odour by distilling under diminished pressure. It boiled at 221—223°/760 mm. (Silkowski's method), and did not solidify at -10° :

0.1976 gave 0.1804 AgCl. Cl=22.59.

C_8H_9OCl requires Cl=22.63 per cent.

β -Naphthol gives a good yield of the ordinary monochloro- β -naphthol. From α -naphthol, which has not hitherto been directly chlorinated, a mixture of monochloro-derivatives is obtained; they are being investigated.

Solubility of 2:4-Dichloroacetanilide and p-Nitroacetanilide in Acetic Acids.—In both cases solutions of the anilides were prepared at 100°, and then placed in a bath at 16°, when some anilide separated. After two hours, given volumes of the solutions were

withdrawn, diluted to 10 per cent. acetic acid, and the anilide extracted with chloroform. The chloroform was evaporated at a low temperature, and the residual anilide weighed. As an alternative, the chloroform extract was mixed with glacial acetic acid, and the anilide converted into chloroamine by bleaching powder, which was titrated after evaporation of the chloroform (compare Edwards and Orton, this vol., p. 1181). To determine the solubility in 50 per cent. acetic acid, the saturated solution in glacial acetic acid was diluted, and an aliquot part withdrawn after keeping at 16° for some hours.

2:4-Dichloroacetanilide:—Five c.c. of glacial acetic acid solution yielded 0.3448 gram of anilide. Solubility, 6.45 per 100 c.c.

Five c.c. of glacial acetic acid solution yielded 0.3163 gram. Solubility, 6.3 per 100 c.c.

Five c.c. of solution in 50 per cent. acetic acid yielded 0.0414 gram. Solubility, 0.83 per 100 c.c.

p-Nitroacetanilide:—Ten c.c. of glacial acetic acid solution yielded 0.0827 gram of anilide. Solubility, 0.83 per 100 c.c.

Twenty c.c. of solution in 50 per cent. acetic acid yielded 0.0754 gram. Solubility, 0.38 per 100 c.c.

Preparation of s-Trichloroaniline:—Five grams of 2:4-dichloroaniline (prepared by hydrolysing the acetyl derivative with 10 per cent. aqueous hydrochloric acid) are dissolved in 50 c.c. of glacial acetic acid, and added to a solution of one equivalent (6.6 grams) of acetylchloroamino-*p*-nitrobenzene in 50 c.c. of acetic acid to which 0.02 c.c. of 20 per cent. hydrochloric acid (1/50th gram-molecule) has been added. The action is very rapid, and some slight colour develops. Part of the nitroacetanilide (see p. 1186) separates, and the remainder, together with some trichloroaniline, on dilution to 50 per cent. acetic acid. The remainder of the aniline is precipitated on further dilution. The insolubility of the anilide permits of the extraction of the aniline by warm alcohol. The yield of pure aniline is over 80 per cent., and there is none of that difficulty in removing colouring matter which is met with in the ordinary method of chlorination.

The thanks of the authors are due to the Government Grant Committee of the Royal Society for the grant which has partly defrayed the cost of this investigation.

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BANGOR.

CXXIX.—*Some Reactions of ω -Bromomethylfurfuraldehyde.*

By WILLIAM FRANCIS COOPER, B.A. (Cantab) and
WALTER HAROLD NUTTALL, F.I.C.

FENTON (Trans., 1898, **73**, 554) showed that ω -bromomethylfurfuraldehyde can condense with malonic esters in presence of alkali hydroxides or sodium ethoxide, giving a product which exhibits a blue fluorescence in solution, and that the reaction is so delicate that it may be used for the detection of traces of hexoses.

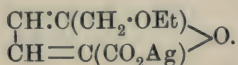
At Dr. Fenton's suggestion, the authors commenced an investigation of this reaction, and have continued the study of the properties of ω -bromomethylfurfuraldehyde.

The isolation of the fluorescent compound or compounds proved to be a matter of exceptional difficulty, as the course of the reaction appeared to be very erratic, and the same products were rarely obtained, even under what seemed to be identical conditions. For this reason, the preparation of new methylfurfuraldehyde derivatives became necessary, and unexpected products were obtained in two instances. These are described in the present communication.

I. *Action of ω -Bromomethylfurfuraldehyde on Silver Cyanide in Presence of Alcohol.*

An attempt to prepare the ω -nitrile or *iso*-nitrile by replacing the bromine by cyanogen by means of potassium or silver cyanide in alcoholic solution led to quite unexpected results; silver bromide was formed, but hydrogen cyanide distilled over quantitatively with the alcohol.

The product, after the removal of the alcohol and hydrogen cyanide, was a dark-coloured oil, which gave an oily precipitate with phenylhydrazine acetate, and which was readily oxidised with silver oxide, giving the crystalline *silver salt of ω -ethoxymethylpyromucic acid*:



On further examination, the oily product which gave the silver salt, was proved to be ω -ethoxymethylfurfuraldehyde. Its formation can only be explained by the interaction of the bromomethylfurfuraldehyde with the alcohol; the hydrogen bromide so liberated acts on the silver cyanide, and hydrogen cyanide is thus formed. Having regard to the extreme reactivity of the bromine in bromomethyl-

furfuraldehyde (compare Fenton and Gostling, Trans., 1899, 75, 427, 430, who showed that the bromine is quantitatively precipitated by alcoholic silver nitrate), such a reaction is intelligible.

That such is the correct explanation is most probable from the fact that, when an alcoholic solution of bromomethylfurfuraldehyde is allowed to evaporate in a vacuum desiccator, hydrogen bromide is liberated; further, when an alcoholic solution of bromomethylfurfuraldehyde is boiled, it rapidly becomes acid. *o*-Ethoxymethylfurfuraldehyde may be most conveniently prepared by this method if means are taken to remove the hydrogen bromide as soon as it is formed, so that polymerisation and formation of humus cannot result. Thus, if an absolute alcoholic solution of bromomethylfurfuraldehyde is boiled with an excess of calcium carbonate, a good yield of ethoxymethylfurfuraldehyde is obtained. Even in the cold there is a considerable reaction and evolution of carbon dioxide. This method of formation is analogous to that described by Fenton and Gostling (Trans., 1899, 75, 431) for the preparation of *o*-hydroxymethylfurfuraldehyde by heating bromomethylfurfuraldehyde in water in the presence of barium carbonate.

The reaction product from alcoholic bromomethylfurfuraldehyde and calcium carbonate on purification and fractionation gives a liquid boiling between 235° and 240°, which analysis and molecular-weight determination show to be *o*-ethoxymethylfurfuraldehyde. The liquid has all the properties of an aldehyde, and gives crystalline *phenyl*- and *p*-bromophenyl-hydrazones.

On oxidation with silver oxide, *o*-ethoxymethylfurfuraldehyde gives a crystalline silver salt, identical with that obtained by the oxidation of the product of interaction of bromomethylfurfuraldehyde and silver cyanide in alcoholic solution.

Both silver salts on acidification yield the same crystalline acid, which was proved to be *o*-ethoxymethylpyromucic acid.

The bromine atom in bromomethylfurfuraldehyde is thus so reactive that it will react with ethyl alcohol directly, and the reaction appears to be a general one. For example, when bromomethylfurfuraldehyde is boiled in methyl-alcoholic solution with excess of calcium carbonate, *o*-methoxymethylfurfuraldehyde is produced. The aldehyde itself was not actually isolated, but was oxidised directly with silver oxide to *o*-methoxymethylpyromucic acid.

An attempt to convert the methoxy-aldehyde into the corresponding methoxy-acid by oxidation with alkaline permanganate gave an acid almost insoluble in water, and quite unlike the acid expected. This acid sublimes on heating, and on warming with ferric chloride gives a transparent jelly. It is, therefore, probably

dehydromucic acid (furan-2:5-dicarboxylic acid). Its preparation by a somewhat similar method, namely, by the oxidation of ω -chloromethylfurfuraldehyde, has already been described by Fenton and Robinson (Trans., 1909, **95**, 1339).

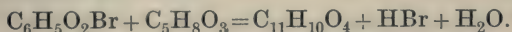
By boiling bromomethylfurfuraldehyde with benzyl alcohol in the presence of calcium carbonate, a clear, yellow oil was produced, which boiled at 301—303°, and had the empirical formula $C_{23}H_{22}O_2$. (Benzyloxymethylfurfuraldehyde has the empirical formula $C_{18}H_{12}O_3$.) The constitution of this compound has not been satisfactorily determined, and the authors are engaged in investigating it.

II. Action of Barium Carbonate on ω -Bromomethylfurfuraldehyde and Water.

In repeating Fenton and Gostling's preparation (*loc. cit.*) of ω -hydroxymethylfurfuraldehyde by boiling ω -bromomethylfurfuraldehyde with water in the presence of barium carbonate, the present authors observed that under certain conditions a beautiful yellow, crystalline product, $C_{11}H_{10}O_4$, is produced, which melts at 111.5—112°.

It was first supposed that this compound might be identical with the anhydride, $C_{12}H_{10}O_5$, obtained by Kiermayer (*Chem. Zeit.*, 1895, **19**, 100) by eliminating one molecule of water from two molecules of hydroxymethylfurfuraldehyde. Kiermayer's anhydride melts at 112°, and is strongly aldehydic in character. It combines directly with two molecules of aniline and phenylhydrazine. No such combinations could be brought about with the authors' compound. Kiermayer's compound is insoluble in benzene or acetic acid, and readily reduces both ammoniacal silver nitrate and Fehling's solution. Further, the two compounds give somewhat different colour reactions with phenols, and a mixture of the two melts very indistinctly at 90—95°, showing that they were not identical.

A substance possessing the formula $C_{11}H_{10}O_4$ might conceivably be obtained from one molecule of bromomethylfurfuraldehyde and one molecule of lævulic acid, by loss of one molecule each of hydrogen bromide and water:



Since ω -bromomethylfurfuraldehyde on boiling with water gives ω -hydroxymethylfurfuraldehyde and hydrogen bromide, and ω -hydroxymethylfurfuraldehyde and mineral acids give lævulic and formic acids (Düll, *Chem. Zeit.*, 1895, **19**, 166, 217; Kiermayer, *ibid.*, 1003), the above reaction is a very possible one. If the yellow,

crystalline compound is a condensation product of ω -bromomethylfurfuraldehyde with lævulic acid, the addition of lævulic acid to the ω -bromomethylfurfuraldehyde and water before heating and adding barium carbonate should give a greatly increased yield of yellow crystals. Investigation shows that the addition of an equivalent quantity of lævulic acid increases the yield by about 50 per cent. Numerous experiments have also been carried out to bring about the formation of the crystals by the condensation of ω -hydroxymethylfurfuraldehyde and lævulic acid, but without success. Further investigation is therefore necessary before the constitution of this compound can be established.

EXPERIMENTAL.

ω -Bromomethylfurfuraldehyde was prepared from lævulose by the action of hydrogen bromide in chloroform solution (compare Fenton and Gostling, *Trans.*, 1899, **75**, 425). The mixture was heated on a water-bath under a reflux condenser for one hour, cooled, and excess of anhydrous sodium carbonate added. It was found advisable to allow the product to remain overnight over sodium carbonate, as by this means a much purer preparation was obtained. The chloroform solution was filtered off, and the solvent removed by distillation at 50° under diminished pressure. The residual oil, on cooling, usually solidified to a mass of large needles, and further purification was not essential, but recrystallisation from dry ether, free from alcohol, was generally considered advisable.

Action of Silver Cyanide on ω -Bromomethylfurfuraldehyde in Alcoholic Solution.

A weighed quantity of ω -bromomethylfurfuraldehyde was dissolved in absolute ethyl alcohol with gentle warming, and the equivalent amount of well-washed and dried silver cyanide added. The mixture was heated on the water-bath for one to two hours, and allowed to cool; the precipitated silver bromide was collected, and well washed with absolute alcohol.

The filtrate was very dark coloured, and had a strong odour of hydrogen cyanide. The alcohol was distilled off on a water-bath, when the hydrogen cyanide passed over completely at the same time. The ethoxymethylfurfuraldehyde may be isolated by extraction with ether; or it may be distilled in a current of steam, and separated from the aqueous distillate by means of ether.

Interaction of ω -Bromomethylfurfuraldehyde and Ethyl Alcohol.

ω -Bromomethylfurfuraldehyde, purified by recrystallisation from dry ether, was dissolved in absolute alcohol; excess of finely powdered calcium carbonate was added, and the mixture heated on the water-bath under a reflux condenser. Since it was not possible to test the completion of the reaction by means of silver nitrate, use was made of Fenton's test, the boiling being continued until no fluorescence was obtained when a few drops of the reaction mixture were mixed with malonic ester and alcoholic potassium hydroxide.

After cooling, the excess of calcium carbonate was filtered off, and the alcohol removed by distillation. The residue was diluted with water to dissolve the calcium bromide, and the solution completely extracted with ether. After removing the ether, an oil was obtained which was distilled under diminished pressure; most of the oil distilled below $145^{\circ}/34$ mm., and the distillate was then fractionated under the atmospheric pressure. The following fractions were collected: up to 90° ; $90-100^{\circ}$; $100-220^{\circ}$; $220-225^{\circ}$; $225-230^{\circ}$; $230-235^{\circ}$; $235-240^{\circ}$.

The residue in the flask was very dark and viscous, and not completely soluble in ether; it was probably a polymerised product, as the aldehyde polymerises very easily. Owing to this fact, it was decided not to attempt a finer fractionation.

In order to ascertain which fraction contained the desired substance, the molecular weights of the fractions $220-225^{\circ}$ and $235-240^{\circ}$ were determined by the cryoscopic method, using benzene as solvent.

Fraction.	Weight of solvent, grams.	Weight of substance, gram.	Depression of freezing point.	M. W.
$220-225^{\circ}$	I. 21.52	0.2779	0.490°	131.8
$220-225$	II. 21.52	0.5936	0.997	130.3
$235-240$	I. 21.24	0.5947	0.907	154.3
$235-240$	II. 22.52	0.5708	0.827	153.2

$C_8H_{10}O_3$ requires M. W. = 154. The fraction $235-240^{\circ}$ was therefore analysed.

I. 0.1718 gave 0.3923 CO_2 and 0.1038 H_2O . C = 62.28; H = 6.71.

II. 0.1660 „ 0.3824 CO_2 „ 0.0987 H_2O . C = 62.70; H = 6.66.

$C_8H_{10}O_3$ requires C = 62.34; H = 6.50 per cent.

 *ω -Ethoxymethylfurfuraldehyde.**

ω -Ethoxymethylfurfuraldehyde, as obtained by either of the two foregoing methods, is a yellow oil, $D_{15.5}^{15.5}$ 1.1096, readily soluble in the

* Since this work on ω -ethoxymethylfurfuraldehyde was carried out, Erdmann (*Ber.*, 1910, 43, 2391) in his paper on ω -hydroxymethylfurfuraldehyde mentions the

usual organic solvents; it is soluble in hot petroleum, but insoluble in cold, and is moderately soluble in water. If rapidly distilled, it boils without decomposition under the ordinary pressure at 235—240°, but prolonged heating induces polymerisation. Under 35 mm. pressure it boils at 145°.

The substance shows the usual properties of an aldehyde. It is readily oxidised by silver oxide or Fehling's solution, and restores the colour to Schiff's reagent. With aniline acetate paper it gives a bright yellow colour. With β -naphthylamine in glacial acetic acid (1:4) a yellow colour is produced, similar to that given by hydroxymethylfurfuraldehyde and the same reagent. With an alcoholic solution of thymol and a few drops of concentrated sulphuric acid, a fine magenta colour is developed. An alcoholic solution of phloroglucinol gives, in the presence of concentrated sulphuric acid, a fine reddish-purple colour with the ethoxy-aldehyde, and a greenish-yellow with furfuraldehyde.

The *phenylhydrazone* was obtained as a pink, oily precipitate, which solidified after decanting the supernatant liquid, washing the residual oil by decantation, drying it by warming over a flame with stirring, and then scratching with a glass rod. Once it has been obtained in the solid condition, it can be recrystallised from various solvents. The most convenient of these is light petroleum, from which it crystallises in long, slender, yellow needles, melting at 55.5—56.2°:

0.1928 gave 0.4847 CO₂ and 0.1172 H₂O. C=68.56; H=6.75.

0.5069 „ 50.0 c.c. N₂ (moist) at 8.9° and 754.9 mm. N=11.77.

C₁₄H₁₆O₂N₂ requires C=68.85; H=6.50; N=11.48 per cent.

The *p-bromophenylhydrazone* crystallises in shining silken needles, which soften at 103°, and melt at 104—105°.

ω -Ethoxymethylpyromucic Acid.

ω -Ethoxymethylfurfuraldehyde, prepared by either of the two methods described, is mixed with water, and heated with a large excess of freshly precipitated silver oxide for three hours, and filtered. The residue is washed with boiling water until no more silver salt is extracted. The yellow filtrate crystallises readily on cooling in small, nodular, grey crystals.

The *silver* salt is moderately soluble in hot water, but not very readily in cold. When recrystallised several times from water, it is

formation of ω -ethoxymethylfurfuraldehyde by precipitating an alcoholic solution of bromomethylfurfuraldehyde with alcoholic silver nitrate, but he gives no details or properties.

obtained in colourless, shining nodules. It can also be purified by precipitation from its aqueous solution by absolute alcohol:

0.2274 gave 0.2896 CO_2 , 0.0702 H_2O , and 0.0856 Ag. $\text{C}=34.73$; $\text{H}=3.43$; $\text{Ag}=39.00$.

$\text{C}_8\text{H}_9\text{O}_4\text{Ag}$ requires $\text{C}=34.65$; $\text{H}=3.25$; $\text{Ag}=38.98$ per cent.

ω -Ethoxymethylpyromucic acid was prepared from the silver salt by dissolving the latter in hot water, and precipitating the silver with sodium carbonate solution. The silver carbonate was removed, and the filtrate, after concentrating, was acidified with sulphuric acid (1:3) and extracted with chloroform, in which the small quantity of dehydromucic acid, also formed, is insoluble. The chloroform extract was dried, and evaporated, when a yellow syrup remained, which after some days solidified to a mass of needles. These, after being collected and washed with ether, became practically white.

The acid can be purified by dissolving in dry ether and adding dry petroleum to the solution. As the ether slowly evaporates, the acid separates in small, shining needles. The most convenient method of purification is crystallisation from carbon disulphide, or by precipitation from chloroform solution with petroleum; the product is obtained in this way in very long, shining needles, melting at $57.5-58.5^\circ$:

0.2270 gave 0.4705 CO_2 and 0.1212 H_2O . $\text{C}=56.53$; $\text{H}=5.96$.

$\text{C}_8\text{H}_{10}\text{O}_4$ requires $\text{C}=56.47$; $\text{H}=5.88$ per cent.

The acid is also soluble in benzene, alcohol, or water. Solutions of its ammonium salt give no precipitate with calcium chloride, lead acetate, basic lead acetate, or copper sulphate.

ω -Methoxymethylpyromucic Acid.

ω -Methoxymethylfurfuraldehyde was prepared by boiling bromomethylfurfuraldehyde in methyl-alcoholic solution with calcium carbonate, and proceeding as in the preparation of the ethoxy-compound. The aldehyde was not isolated, but, after the removal of the calcium bromide, was oxidised with silver oxide. The acid was prepared from the silver salt in the usual manner, and was extracted by chloroform. It was best purified by precipitating from chloroform with petroleum:

0.1955 gave 0.3850 CO_2 and 0.0913 H_2O . $\text{C}=53.71$; $\text{H}=5.18$.

0.2960 „ 0.4413 AgI. $\text{OMe}=19.67$.

$\text{C}_6\text{H}_5\text{O}_3\cdot\text{OMe}$ requires $\text{C}=53.84$; $\text{H}=5.13$; $\text{OMe}=19.87$ per cent.

The properties of *ω -methoxymethylpyromucic acid* are similar to those of the ethoxy-compound. It crystallises in long, silken needles, which melt at $67.5-68.5^\circ$.

Preparation of the Compound $C_{11}H_{10}O_4$.

In order to obtain this compound, ω -bromomethylfurfuraldehyde is melted under water, the mixture heated to 60° , and barium carbonate added little by little, care being taken to maintain the solution always slightly acid. The aqueous solution quickly becomes coloured a canary-yellow, and the melted aldehyde gradually passes into solution. When this occurs, a large excess of barium carbonate is added, the mixture heated nearly to boiling, and filtered hot. The yellow filtrate deposits an oil on cooling, which, on remaining overnight, becomes a mass of crystals. The yield varies greatly, and is rarely large. It appears to depend largely on the temperature to which the reaction mixture is heated. The compound, which usually crystallises in canary-yellow needles, but sometimes in plates, may be crystallised from hot water, but more readily from hot alcohol or benzene. It is best purified by dissolving in glacial acetic acid, and precipitating with dry petroleum, when it is obtained in microscopic needles. These are then recrystallised from carbon tetrachloride. The compound melts at 111.5 — 112° . Its solutions in all solvents are yellow, possessing a slight green tinge. It is neutral to litmus, but sodium carbonate solution extracts it from an ethereal solution. The crystals do not readily reduce either ammoniacal silver nitrate or Fehling's solution, considerable boiling being necessary. With phenylhydrazine acetate, a very slight precipitate is obtained after some time. The compound does not restore the colour to Schiff's reagent. From these reactions it does not appear to be aldehydic in nature; neither does it contain bromine:

0.1902 gave 0.4471 CO_2 and 0.0828 H_2O . $C = 64.11$; $H = 4.83$.

0.1909 „ 0.4477 CO_2 „ 0.0832 H_2O . $C = 63.96$; $H = 4.84$.

0.921 in 29.2 acetic acid gave $\Delta t - 0.12$. M.W. = 204.

$C_{11}H_{10}O_4$ requires $C = 64.08$; $H = 4.85$ per cent. M.W. = 206.

THE COOPER LABORATORY FOR ECONOMIC RESEARCH,
WATFORD.

FARADAY LECTURE.

(Delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution, on Wednesday, June 14th, 1911.)

The Fundamental Properties of the Elements.

By THEODORE WILLIAM RICHARDS.

WE meet to-night to honour the memory of Michael Faraday. It is fitting that we should come to this historic place; for here were his home and his laboratory, and in this room he lectured. Science is one of the great influences promoting the solidarity of mankind; it is world-embracing, and recognises no bounds of nationality. Faraday's work especially was a message to the whole world, and has grown into a priceless heritage for all humanity. Therefore, from time to time the generous guardians of this famous lectureship have called chemists and physicists from many lands to honour his unique genius. England, Germany, France, Italy, Russia have all sent eminent representatives; and now from across the sea there comes a pilgrim who is proud indeed to bring the homage of the New World to this shrine of cherished memories. The many ties—kindred blood, mutual sympathies, like ideals, and a common language—which bind together our two nations add especial pleasure to the fulfilment of the trust.

The mystery that enshrouds the ultimate nature of the physical universe has always stimulated the curiosity of thinking man. Of old, philosophers sought to solve the cosmic problem by abstract reasoning, but to-day we agree that the only hope of penetrating into the closely guarded secret lies in the precise estimation of that which is tangible and visible. Knowledge of the actual behaviour of material and of energy provides the only safe basis for logical inference as to the real essence of things. Faraday was deeply imbued with this conviction; and it is widely recognised as the basis of all modern experimental science. The subject of my lecture to-night concerns the methods and general results of several extended series of investigations, planned with the hope of adding a little to the foundations of human knowledge by means of careful experiment.

At the outset let me remind you of an old saying of Plato's, for it sounds the keynote of the lecture: "If arithmetic, mensuration, and weighing be taken away from any art, that which remains will not be much."* In other words, the soundness of all important conclusions of mankind depends on the definiteness of the data on which they are based.

* Plato, *Philebus* (trans. Jowett), 1875, Vol. IV., p. 104.

Lord Kelvin said: "Accurate and minute measurement seems to the non-scientific imagination a less lofty and dignified work than looking for something new. But nearly all the grandest discoveries of science have been the rewards of accurate measurement and patient, long-continued labour in the minute sifting of numerical results."* The more subtle and complicated the conclusions to be drawn, the more exactly quantitative must be the knowledge of the facts.

Measurement is a means, not an end. Through measurement we obtain data full of precise significance, about which to reason; but indiscriminate measurement will lead nowhere. We must choose wisely the quantities to be measured, or else our time may be wasted.

Among all quantities worthy of exact measurement, the properties of the chemical elements are surely some of the most fundamental, because the elements are the vehicles of all the manifold phenomena within the range of our perception.

Weight is clearly one of the most significant of these properties. The eighty or more individual numbers which we call the atomic weights are perhaps the most striking of the physical records Nature has given us concerning the earliest stages of the evolution of the universe. They are mute witnesses of the first beginnings of the cosmos out of the chaos, and their significance is one of the first concerns of the chemical philosopher.

Mankind is not yet in a position to predict any single atomic weight with exactness. Therefore the exact determination of atomic weights rests upon precise laboratory work; and in order to arrive at the real values of these fundamental constants, chemical methods must be improved and revised so as to free them from systematic or accidental errors.

What, now, are the most important precautions to be taken in such work? These are worthy of brief notice, because the value of the results inevitably depends upon them. Obvious although they may be, they are often disregarded.

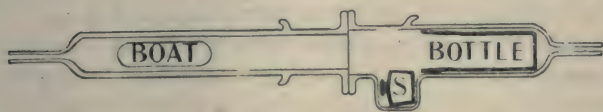
In the first place, each portion of substance to be weighed must be free from the suspicion of containing unheeded impurities; otherwise its weight will mean little. This is an end not easily attained, for liquids often attack their containing vessels and absorb gases, crystals include and occlude solvents, precipitates carry down polluting impurities, dried substances cling to water, and solids, even at high temperatures, often fail to discharge their imprisoned contaminations.

* Sir W. Thomson (Lord Kelvin), *Address to British Association*, Aug., 1871, *Life*, II. 600.

In the next place, after an analysis has once begun, every trace of each substance to be weighed must be collected and find its way in due course to the scale-pan. The trouble here lies in the difficulty in estimating, or even detecting, minute traces of substances remaining in solution, or minute losses by vaporisation at high temperatures.

In brief, "the whole truth and nothing but the truth" is the aim. The chemical side of the question is far more intricate and uncertain than the physical operation of weighing. For this reason it is neither necessary nor advisable to use extraordinarily large amounts of material; from five to twenty grams in each experiment is usually enough. The exclamation, "What wonderfully fine scales you must have to weigh atoms," indicates lack of knowledge; the real difficulties precede the introduction of the substance into the balance case.* Every substance must be assumed to be impure, every reaction must be assumed to be incomplete, every measurement must be assumed to contain error, until proof to the contrary

FIG. 1.



can be obtained. Only by means of the utmost care, applied with ever-watchful judgment, may the unexpected snares which always lurk in complicated processes be detected and rendered powerless for evil.

Among all the possibilities of error, the unsuspected presence of water is perhaps the most frequent and most insidious. Hence I shall show you a device for overcoming this potent source of confusion, a device which has played a great rôle in the recent researches concerning atomic weights at Harvard, and is in large measure responsible for such value as the results may possess. The instrument† enables one to dry, enclose, and weigh an anhydrous substance in such a manner as to preclude the admission of a trace of water from the atmosphere; it might well find applications in

* Richards, *Methods Used in Precise Chemical Investigation*, published by the Carnegie Inst. of Washington, 1910, No. 125, p. 97.

† Richards, *Zeitsch. anorg. Chem.*, 1895, **8**, 267; also Richards and Parker, *ibid.*, 1897, **13**, 86. The form of apparatus shown in this diagram is slightly different from the original arrangement, although the main idea is the same. The flat ground joint between quartz and glass allows for their different coefficients of expansion, and makes a quartz tube interchangeable with any other, in case of breakage.

every quantitative laboratory. The simple device consists of a quartz ignition tube fitted to a soft-glass tube which has a projection or pocket in one side (Fig. 1). A weighing-bottle is placed at the end of the latter tube, and its stopper in the pocket. The boat containing the substance to be dried is heated in the quartz tube, surrounded by an atmosphere consisting of any desired mixture of gases. These gases are displaced, after partial cooling, first by nitrogen, and then by pure dry air, and the boat is pushed past the stopper into the weighing-bottle, the stopper being then forced into place, and the substance thus shut up in an entirely dry atmosphere. The weighing-bottle may now be removed, placed in an ordinary desiccator, and weighed at leisure. The substance is really dry, and its weight has definite significance.

Mention may be made also of another instrument, which likewise has greatly facilitated the recent work at Harvard, namely, the "nephelometer." * With the nephelometer, minute traces of suspended precipitate may be approximately determined from the brightness of the light they reflect. The construction is very simple. Two test-tubes, near together and slightly inclined toward one another, are arranged so as to be partly shielded from a bright source of light by sliding screens. The tubes are observed from above through two thin prisms, which bring their images together and produce an appearance resembling that in the familiar half-shadow polarimeter. The unknown quantity of dissolved substance is precipitated as a faint opalescence in one tube by means of suitable reagents; and a known amount, treated in exactly the same way, is prepared in the other. Each precipitate reflects the light; the tubes appear faintly luminous. If the tubes show like tints to the eye when the screens are similarly placed, the precipitates may be presumed to be equal in amount. In case of inequality of appearance, the changed positions of the screens necessary to produce equality of tint give a fairly accurate guide as to the relative quantities of precipitate in the two tubes. Traces of substance, which are too attenuated to be caught on any ordinary filter, may thus be estimated.

The two errors obviated by these simple devices—namely, the presence of residual water and the loss of traces of precipitate respectively—have perhaps ruined more previous investigations than any other two causes, unless the inclusion of foreign substances by precipitates may be ranked as an equal vitiating effect. But these are merely details; the scope and method of the recent work on this subject at Harvard (in the course of which thirty atomic

* Richards, *Zeitsch. anorg. Chem.*, 1895, **8**, 269; Richards and Wells, *Amer. Chem. J.*, 1904, **31**, 235; Richards, *ibid.*, 1906, **35**, 510.

weights have been re-determined) may be seen in their full bearing only in the original papers.*

That the atomic weights may be connected by precise mathematical equations seems highly probable; but although many interesting attempts have been made to solve the problem,† the exact nature of such relationships has not yet been discovered. No attempt which takes liberties with the more certain of the observed values is worthy of much respect. It seems to me that the discovery of the ultimate generalisation is not likely to occur until many atomic weights have been determined with the greatest accuracy. No trouble being too great to attain this end, the Harvard work will be continued indefinitely, and attempts will be made to improve its quality, for the discovery of an exact mathematical relationship between atomic weights would afford us an immeasurably precious insight into the ultimate nature of things.

But weight is only one of the fundamental properties of an element. Volume is almost, if not quite, as important in its own way, although far more variable and confusing. All gases, indeed, approach closely to a simple relationship of volumes, defined by the law of Gay Lussac and the rule of Avogadro, and well known to you all. In the liquid and solid state, however, great irregularities are manifest, and very little system as regards volume is generally recognised.

About twelve years ago, the study of such small irregularities as exist among gases led me to the suspicion of a possible cause for the greater irregularities in liquids and solids.‡ On applying van der Waals's well-known equation to several gases, in some tentative and unpublished computations, it seemed clear that the quantity b is not really a constant quantity, but is subject to change under the influence of both pressure and temperature. This conclusion has also been reached independently by van der Waals himself.||

* An important part in these researches has been taken by G. P. Baxter, and many able students also have assisted the author in the work. A complete bibliography is given in *Publ. Carnegie Inst. of Washington*, 1910, No. 125, 91. Most of the papers are reprinted in full in a volume entitled, *Experimentelle Untersuchungen über Atomgewichte*, by the author and his collaborators (Hamburg, 1909). The Carnegie Institution of Washington has generously subsidised the work in recent years.

† See especially Rydberg, *Zeitsch. anorg. Chem.*, 1897, 14, 66.

‡ Richards, "The Significance of Changing Atomic Volume," *Proc. Amer. Acad.*, 1901, 37, 1; 1902, 37, 300; 1902, 38, 293; 1904, 39, 581; *Zeitsch. physikal. Chem.*, 1902, 40, 169, 597; 1903, 42, 129; 1904, 49, 15.

|| van der Waals, *Zeitsch. physikal. Chem.*, 1903, 28, 257. His earlier publication on this topic (*Proc. R. Akad. Wetensch. Amsterdam*, 1898, 29, 138) was unknown to me at that time. See also Lewis, *Proc. Amer. Acad.*, 1899, 35, 21.

But if the quantity b (supposed to be dependent upon the space actually occupied by the molecules) is changeable, are not the molecules themselves compressible? *

The next step in the train of thought is perhaps equally obvious. If changes in the bulk of molecules are to be inferred even from gases, may not the expansion and contraction of solids and liquids afford a much better clue to the relative expansion and contraction of these molecules?

Most physical chemists refer all changes in volume to changes in the extent of the *empty space* between the molecules. But are there, after all, any such empty spaces in solids and liquids? Solids do not behave as if the atoms were far apart within them; porosity is often conspicuous by its absence. Take, for instance, the case of glass; the careful experiments of Landolt on the conservation of weight † show that glass is highly impermeable to oxygen, nitrogen, and water for long periods. Such porosity as occurs in rigid, compact solids usually permits the passage only of substances which enter into the chemical structure of the solids themselves. Thus, nitrogen cannot free itself from imprisonment within hot cupric oxide, although oxygen can escape ‡; again, water cannot evaporate into even the driest of atmospheres from accidental incarceration in crystals lacking water of crystallisation. || Palladium, on occluding hydrogen, is obliged to expand its bulk in order to make room for even this small addition to its substance. The behaviour of platinum, nickel, and iron is probably analogous, although less marked. § Fused quartz, impermeable when cold, allows of the passage of helium and hydrogen at high temperatures ¶; but most other gases seem to be refused admission, and very many solid substances appear to act as effective barriers to the passage of even hydrogen and helium, especially when cold. In these cases, as in so many others, the so-called "sphere of influence" of the atom is the actual boundary by which we know the atom and measure its behaviour.** Why not call this the actual bulk of the atom?

* van der Waals speaks cautiously, but with some conviction, as to the probable compressibility of the molecules on p. 283 of the paper cited above.

† H. Landolt, "Über die Erhaltung der Masse bei chem. Umwandlungen," *Abhandlung der königl. preuss. Akad. der Wissenschaften*, 1910.

‡ Richards, *Zeitsch. anorg. Chem.*, 1892, **1**, 196; *Proc. Amer. Acad.*, 1893, **28**, 200. || Baker and Adlam, *Trans.*, 1911, **99**, 507.

§ Richards and Behr, *Publ. Carnegie Inst.*, 1906, **61**.

¶ Jacquerod and Perrot, *Compt. rend.*, 1907, **144**, 135.

** Since these ideas were first advanced, Barlow and Pope have brought forward much interesting evidence concerning the significance of the volumes of solids and liquids, which supports the idea that the atoms are closely in contact with one another (*Trans.*, 1906, **89** 1675; 1907, **91**, 1150; 1908, **93**, 1528; 1910, **97**, 2308).

From another point of view, the ordinary conception of a solid has always seemed to me little short of an absurdity. A gas may very properly be imagined with moving particles far apart, but what could give the rigidity of steel to such an unstable structure? The most reasonable conclusion, from all the evidence taken together, seems to be that the interstices between atoms in solids and liquids must usually be small even in proportion to the size of the atoms themselves, if, indeed, there are any interstices at all.

Very direct and convincing evidence of another sort is at hand. The idea that atoms may be compressible receives striking confirmation from a recent interesting investigation of Grüneisen* concerning the small effect of low temperatures on the compressibility of metals. The average compressibility of aluminium, iron, copper, silver, and platinum falls off only seven per cent. between the temperature of the room and that of liquid air. Extrapolation of the curves indicates that at the absolute zero very little further diminution should occur. As far as we can guess, therefore, the hard metals are almost as compressible at the absolute zero as at room temperatures. But at the absolute zero all heat-vibration is supposed to stop; hence this remaining compressibility must needs be ascribed to the atoms themselves.

If the atoms are compressible, all mathematical reasoning which assumes them to be incompressible rests upon a false basis. The kinetic theory of *gases* remains unmolested by these considerations, except as they indicate the changeability of b in the equation of van der Waals, but the new views affect seriously the application of this equation to solids and liquids.

Let us proceed to trace a few of the outcomes of our hypothesis. If atoms may really be packed closely together, the volumes of solids and liquids should afford valuable knowledge concerning the relative spaces occupied by the atoms themselves under varying conditions. The densities of solids and liquids then assume a significance far more interesting to the chemical philosopher than before, because they have a more definite connexion with the fundamental nature of things.

An apparent objection at once suggests itself; if the particles in condensed material are really touching one another, how can we account for heat within the material? Would such closely packed atoms be able to vibrate?

The theory of compressible atoms supplies as one of its own

* E. Grüneisen, *Ann. Physik*, 1910, [iv], 33, 1239. The *relative* values for the compressibilities recorded in this investigation are doubtless trustworthy, although the absolute magnitudes are somewhat uncertain because they depend on the rather inadequate theory of elasticity.

corollaries the immediate answer to this question. If atoms are compressible throughout their whole substance, they may contract and expand, or vibrate within themselves, even when their surfaces are prevented from moving by being closely packed together. It is thus possible to conceive of a vibrational effect, even in contiguous atoms, provided we can conceive of these atoms as being elastic throughout all their substance. Agitation sufficient to produce even the Brownian movement might easily exist in such a system.

Clearly there is nothing impossible or obviously contradictory to experimental knowledge in the notion that atoms are compressible; indeed, the old idea of small, hard particles far apart is really more arbitrary and hypothetical than the new conception. The obvious simplicity of the latter is rather in its favour than otherwise, as in Dalton's atomic theory. In general, the more simply an hypothesis interprets the phenomena of nature, the more useful the hypothesis is likely to be, provided, of course, that the interpretation is adequate. The modern philosophy of pragmatism is a good guide in such matters; a theory not obviously illogical should be judged by its usefulness. Let us then test the new hypothesis by applying it to other aspects of physical chemistry.

If pressure produces a change in the sizes of the atoms and molecules themselves, may not the actual volumes of liquids and solids be used as a guide to the unknown internal pressures within them? Cannot we thus discover whether or not chemical affinity exerts pressure in its action? To follow this clue, the simplest possible case was chosen at first, namely, the comparison of the contractions taking place on combining several elements in succession with a single very compressible one. The changes of volume occurring during the formation of oxides were first computed; later, chlorides and bromides were studied. According to the theory of compressible atoms, we should expect to find greater contraction in cases of greater affinity. The diagram (Fig. 2), which depicts typical data concerning certain nearly related chlorides, strongly supports this inference.* One of these lines shows the total change of volume which occurs when a gram-molecule of chlorine combines with the equivalent weight of metal; the other gives the heat evolved during combination. The lines show distinct parallelism; that is to say, reactions evolving much heat manifest great contraction. In cases of this kind, the heat of reaction is usually not very different from the change of free-energy, therefore we may infer that greater *affinity* is associated with greater contraction; and it is but a small leap in the dark to guess that the

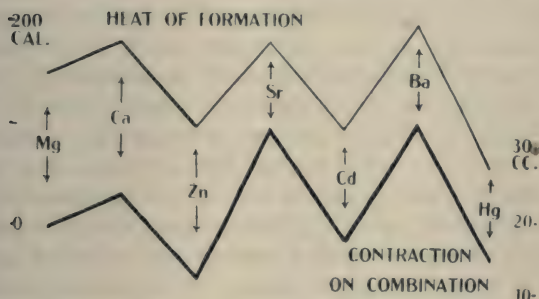
* Richards, *Proc. Amer. Acad.*, 1902, **37**, 399; also especially *J. Amer. Chem. Soc.*, 1909, **31**, 188.

change of volume is *caused* by the pressure of affinity. Since chemical attraction holds two elements firmly together, why should it not exert pressure? And if it exerts pressure, why should not the volume of the system be diminished by this pressure? .

This interpretation is not wholly new. Faraday's great teacher, Davy,* pointed out for the first time a similar fact; namely, that the contraction which takes place on forming the oxide of potassium is greater than the contraction which takes place on forming the oxide of tin, and he ascribed this effect to the well-known differences of affinity in the two cases; but he did not carry the idea further. Long afterwards, Braun,† Mueller-Erbach,‡ Hagemann,|| and

FIG. 2.

COMPARISON of HEATS OF FORMATION of CHLORIDES
and CONTRACTION ON COMBINATION



Traube § independently and apparently without knowledge of each other's work, called attention to other cases of similar relationships.

All of these researches have produced so little effect on the literature of the subject ¶ that they were entirely overlooked during the earlier part of the present investigation. The oversight mattered little, however, because the whole subject needed a fresh attack. Essential factors in the situation had not been noticed by any of these earlier investigators. Affinities, indeed, had been

* Humphry Davy, Collected Works, 1840, 5, 133 (footnote).

† V. Braun, see Johnson, Trans., 1877, 31, 252.

‡ Mueller-Erbach, Ber., 1881, 14, 217, 2043.

|| Hagemann (Private publication, Friedländer, Berlin, 1900).

§ Traube, "Über den Raum der Atome," Ahrens' Sammlung der chem. und chem.-techn. Vorträge, IV., 256.

¶ See, for example, Ostwald's Grundriss der allgemeinen Chemie, 1899, p. 185.

considered, but the nature of the substances on which the affinities act had been overlooked. Evidently the change of volume in any case must depend not only on the intensity of the pressure exerted by the affinity, but also, among other things, on the compressibility of the substances concerned. The greater the compressibility, the greater should be the change of volume caused by a given pressure of affinity. Before any definite conclusion can be drawn, the differences in compressibility must be taken into account.

These thoughts led to the measuring of the compressibilities of a large number of elements and simple compounds. The previously employed methods for solids and liquids being unsatisfactory, a new and highly satisfactory method was devised for the work done at Harvard. Pure mercury is compressed in a suitable tube, measuring both pressure and change of volume, and then most of the mercury is displaced by the substance to be studied, again noting the relationship of pressure to volume. The difference between the compressibility of mercury and that of the substance is then easily calculated. Obviously, in such a method as this, the compressibility of the apparatus itself is eliminated. The relation of volume to pressure is easily determined by causing the mercury meniscus to make electrical contact with a very fine platinum point in a tube of narrow diameter, adding weighed globules of mercury, and noting the corresponding pressures.* Time forbids the description of the details of the procedure.

The compressibilities of thirty-five elements and many simple compounds were studied by this method with sufficient care to leave no doubt as to their relative values. It became at once manifest that the formation of a compound of a compressible element was attended with greater decrease of volume than the formation of a similar compound of a less compressible element, other things being equal.† This is just what the theory leads us to expect, and is a fact inexplicable by any other hypothesis as yet known to me.

Another essential aspect of the theory of compressible atoms is that which concerns cohesion.‡ If the pressure of chemical affinity causes atomic compression, may not the pressure of cohesive affinity also have the same effect? Traube suggested this possibility, but looked at the whole question from a different point of view.¶ The affinity which prevents solids and liquids from vaporis-

* Richards, in collaboration with Stull, Bonnet, Brink, Mathews, Jones, Speyers, *Publ. Carnegie Inst. of Washington*, Nos. 7 and 76; *J. Amer. Chem. Soc.*, 1904, **26**, 399; 1909, **31**, 154; *Zeitsch. physikal. Chem.*, 1904, **49**, 1; 1907, **61**, 77.

† Richards, *Proc. Amer. Acad.*, 1904, **39**, 581.

‡ *Ibid.*

¶ See especially Traube, *Ann. Physik.*, 1897, [iii], **61**, 383; 1901, [iv], **5**, 548; 1902, **8**, 267; 1907, **22**, 519; *Zeitsch. physikal. Chem.*, 1910, **68**, 289; also

ing is generally admitted to produce great internal pressure; must it not tend to compress the molecules into smaller space? Molecules with high cohesive affinity (those of substances hard to volatilise) should be much compressed and possess small volume, whereas molecules with a slight cohesive affinity should be more bulky. Moreover, those molecules already much compressed by their own self-affinity would naturally be but little affected by additional pressure. Thus, as regards two substances otherwise similar, the less volatile one would be less compressible, denser, and possess greater surface tension.* These outcomes of the theory correspond with the facts in a majority of cases thus far studied; for example, *o*-xylene is denser, less volatile, less compressible, and possesses a greater surface tension than either *m*-xylene or *p*-xylene.† Differences of structure and differences of chemical nature sometimes conceal these relations; the parallelism appears most strikingly among isomeric compounds. In brief, the bulk of evidence strongly indicates that cohesiveness as well as chemical affinity exerts pressure in its action, and hence that each plays a part in determining the volumes occupied by molecules.

Thus the computation of the space occupied by either a solid or a liquid becomes a very complex matter. Not only must the various chemical affinities at work be taken into account, but also the cohesive attraction of both factors and products, and the compressibilities over a very wide range of all the substances concerned. Discoverable parallelism in volume changes is to be expected only when one alone of these forces is the chief variable.

The exact mathematical working out of the consequences is very far in the distance, if, indeed, it can ever be attained. This fact does not, however, militate in the least against the plausibility of the idea. Although mankind has not yet been able to devise a method of mathematical analysis which will solve at one stroke the

Walden, *Zeitsch. physikal. Chem.*, 1909, **66**, 385. Their interpretation depends largely on the application of van der Waals' equation and the complicating assumption of a *co-volume*; however, Walden's very recent paper presents a number of interesting and important relations concerning internal pressure, which seem to demand the assumption of atomic compressibility for their explanation.

* Richards and Mathews, *Zeitsch. physikal. Chem.*, 1908, **61**, 449.

† With the help of C. L. Speyers I have determined these constants with great care. The substances were unusually pure, the *p*-xylene freezing at 13.2°. The details will be published as soon as possible. The results are recorded in the following table:

	Boiling point.	Density, 20°/4°.	Surface tension (mg./mm. ; 20°).	Compress- ibility × 10 ⁶ at 20°.
<i>o</i> -Xylene	144.0°	0.8811	3.09	60.0
<i>m</i> -Xylene	139.0	0.8658	2.96	63.5
<i>p</i> -Xylene	136.2	0.8611	2.92	66.2

gravitational relations of three bodies, Nature is not on that account prevented from causing three or more bodies to act on one another with the force of gravity, or astronomers from calculating as nearly as may be the consequences by a process of approximation.

Carried through to its logical conclusion, the idea that atoms are compressible gives one quite a new conception of the molecular mechanics of the universe. The influence of atomic compressibilities may be perceived everywhere, and in most cases each fact seems to fit easily and without constraint into its place in the hypothesis. Even apparent exceptions, such as the abnormal bulk of ice, may be ascribed in a reasonable fashion to superposed effects. A detailed discussion of many applications of the theory is impossible here, but a few may be suggested, in order to make clearer its possibilities.

The satisfying of each valence of an atom would cause a depression on the atomic surface, owing to the pressure exerted by the affinity in that spot. The stronger the affinity, the greater should be this distortion. Evidently this conception gives a new picture of the asymmetric carbon atom, which, combined with four other different atoms, would have upon its surface depressions of four unequal magnitudes, and be twisted into an unsymmetrical tetrahedron. The combining atoms would be held on the *faces* of the tetrahedron thus formed, instead of impossibly perching upon the several peaks. According to this hypothesis, the carbon atom need not be imagined as a tetrahedron in the first place; it would assume the tetrahedral shape when combined with the other four atoms. One can easily imagine that the development of each new valence would change the affinities previously exercised, somewhat as a second depression in the side of a rubber ball will modify a forcibly caused dimple in some other part. Thus a part of the effect which each new atom has on the affinities of the other atoms already present may be explained.

Many other physico-chemical phenomena assume a new aspect when viewed from the standpoint of this idea. New notions of the mechanism of the critical phenomena, surface tension, ductility, malleability, tenacity, and coefficient of expansion are gained. The peculiar relations of material and light, such as magnetic rotation, fluorescence, partial absorption, and so forth, may be referred to the modified vibrations of distorted atoms. The deviations from the exact fulfilment of many older generalisations concerning volume (such as the equation of van der Waals already cited, the comparative volumes of aqueous solutions, especially of electrolytically dissociated substances,* and the variations in the crystal

* Baxter has very recently discussed this matter from the point of view of the theory of compressible atoms (*J. Amer. Chem. Soc.*, June, 1911).

forms of isomorphous substances) are seen to be a foregone conclusion. Moreover, the theory, although not necessarily dependent on the modern belief that atoms are built up of numbers of much smaller corpuscles, is consistent with that belief, for would not such an entity be compressible?

The more closely the actual data are studied, the more plausible the hypothesis of compressible atoms appears. Ten years' experience with its interpretations leads me to feel that the idea is highly suggestive and helpful in stimulating new search after truth and in correlating and codifying diverse facts. By such fruit are hypotheses justified.

The relation between heat of reaction and change of volume stimulates interest in chemical thermodynamics and curiosity as to the mechanism of the output of energy during chemical change. A search for accurate data wherewith to reason about this question soon revealed the uncertain nature of many of the figures. Here, in the domain of thermochemistry, as in those of atomic weights and compressibilities, new methods were needed in order to attain precise results. Accordingly a device was adopted which at one stroke annihilates the pernicious "cooling correction"—the worst foe to accuracy—by merely causing the temperature of the jacket around the calorimeter to change in temperature at the same rate as the calorimeter itself. There are several ways in which this may be accomplished; among these ways the following was chosen as the best method for a chemical laboratory. The calorimeter, enclosed in a slightly larger water-tight vessel, with tubes above—a kind of submarine—is immersed under the surface of dilute crude alkali in a pail. Thermometers inside and out enable one to adjust the temperatures at the same point. The reaction is then started in the calorimeter, and at the same moment and at a corresponding rate acid is dropped into the dilute alkali in the pail, so that the two temperatures inside and out keep pace with one another. Thus there is no loss of heat from the inside vessel; the thermochemical reaction is strictly adiabatic. This method has already been used at Harvard with very encouraging outcome in determining a wide variety of thermochemical data, heats of combustion of hydrocarbons, of solutions of metals in acids and of neutralisation, specific heats of solutions, and also of the elements at very low temperatures, and finally latent heats of evaporation.* It has proved itself especially valuable in the study of slow reactions, where the cooling

* Richards, in collaboration with Henderson, Forbes, Frevert, Mathews, Rowe, Jesse, Burgess, and Jackson, *Proc. Amer. Acad.*, 1905, **41**, 3; 1907, **42**, 573; 1908, **43**, 475; 1911, **46**, 363; *J. Amer. Chem. Soc.*, 1909, **31**, 1275; 1910, **32**, 268, 432, 1176; *Zeitsch. physikal. Chem.*, 1905, **52**, 551; 1907, **59**, 531; 1909, **70**, 414.

correction may become a large portion of the total result. The effort is being made to apply to this experimentation concerning chemical energetics the same degree of care which has recently been attempted in the revision of the atomic weights, and although on account of the greater complexity of the problem the percentage accuracy thus far reached has not equalled that in the case of atomic weights, one cannot help thinking that the proportional gain over previous investigations is perhaps as great in this case as in the other.

In thermochemical reasoning particularly, accurate data possess a significance wholly denied to cruder results. The relations between the heat of formation of organic substances, if determined accurately enough, may be hoped to throw light on organic structure and the nature of valence. Approximate values are of no use at all for such a purpose. Enough has been done already to suggest relations of a highly interesting sort between heats of combustion, heats of evaporation, compressibility, and many other properties; and to add support to the theory of compressible atoms.* Moreover, taken in connexion with more precise knowledge of the free energy of chemical changes, the new results will permit the evaluation of bound energy, and give results which may decide whether or not bound energy is really a simple function of change of heat capacity, as has been more than once intimated.† There is time now only to suggest possibilities, each of which would take hours to elucidate.

How can we collate all the varying properties so as to show their many-sided relationships? How can we piece together the scattered evidence so as to synthesise an adequate conception of the ultimate nature of things? These questions may never be adequately answered, but science must ceaselessly endeavour to solve the problem which they present.

A first step is clearly to find the way in which each property varies in relation to every other. With this in mind, let us appeal to the irregular system of the periodic classification, which formed the subject of the Faraday Lecture by Mendeléeff twenty-two years ago. This mysterious index of uncharted tendencies must hide within itself guiding ideas capable of pointing us onward.

Clearly each property must receive, not merely qualitative, but

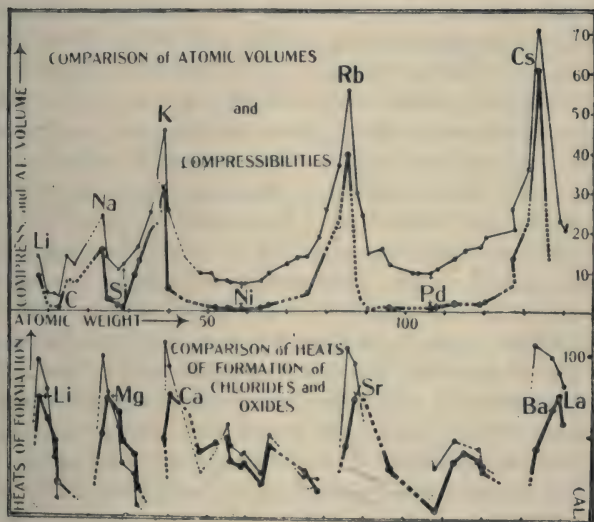
* Richards, *Proc. Amer. Acad.*, 1908, **39**, 581; also *Zeitsch. physikal. Chem.*, 1904, **49**, 15.

† Helmholtz, Lewis, van't Hoff, Nernst and Haber, as well as the author and many others, have contributed to this discussion. An interesting résumé, with references to many of the original papers, will be found in Haber's *Thermodynamics of Technical Gas Reactions* (translated by Lamb), London and New York, 1908.

strictly quantitative treatment. With this in mind, let us compare our various facts by plotting atomic weight in one direction, and all the other properties in another. Then by noting the parallelism or antiparallelism of the wavy lines, many relationships may be traced. The device is not new. Carnelley compared Lothar Meyer's atomic volume curve with that of melting points, and other similar data have been plotted; but the method has not been used to its full extent.

Let us then turn to the diagram (Fig. 3) in which the variations in a number of properties are plotted with relation to the atomic weights. Prominent among the lines is the atomic-volume curve

FIG. 3.



just mentioned. Below it is plotted the almost parallel line depicting the compressibilities of the solid elements as determined at Harvard; these are immediately seen to be, like the atomic volumes, periodic functions of the atomic weights. The parallelism cannot but suggest that atomic volume and compressibility are fundamentally connected; and, indeed, the theory of compressible atoms gives a plausible explanation of the connexion. We should expect the large atomic volumes to be more compressible, because we might infer from their bulk that they are not under as great pressures as the small volumes, and material under slight pressure is likely to be easily compressible. Moreover, the bulky and easily compressible elements are in most cases more easily melted and vola-

tilised than those possessing small volume and slight compressibility. This is just what we might expect; all these properties combine to indicate that the bulky elements have less cohesion than the compact ones.

Next, another set of waves may be considered, representing properties not often depicted in this way. These are the heats of formation of sundry similar compounds, also plotted with relation to the atomic weights. In the third curve are given the heats of combination of chlorine with other elements, and below it a heavy line depicting the heats of the combination of oxygen with these elements, both sets of quantities being expressed in terms of gram-equivalents.

These two run partly parallel with one another; but a deviation in the parallelism appears, which is full of suggestiveness. The peaks of the curves representing oxides shift distinctly to the right of the curve representing chlorides as the atomic weight increases. Lithium marks a maximum with both curves, but the oxygen curve lags greatly at the succeeding peaks, having its maximum with lanthanum at the atomic weight 139,* and shifting over as far as lead above 200. This simple fact standing alone would perhaps mean but little, but other similar facts seem to point in the same direction. For example, the property of electro-positiveness, exhibited by the alkali metals, instead of reappearing in copper, has been carried over with diminished intensity to zinc; and finally, among the higher atomic weights the cusp has deserted mercury (the analogue of zinc) and gone as far afield as thallium. Clearly the rate of progression which determines electro-positiveness has a longer "wave-length" than that which determines valence, if we may describe the periodicity of these zigzag curves as waves. Again, the tendency towards low melting point unquestionably likewise progresses with a longer "wave-length" than most of the other properties. In the first complete period, nitrogen, oxygen, fluorine,

* The essential data for discovering this generalisation, namely, the heats of oxidation of the metals having such affinity for oxygen, are as follows: lithium, 72; sodium, 50; magnesium, 72; potassium, 43; calcium, 76; rubidium, 42; strontium, 71; cesium, 41; barium, 67, and lanthanum, 74. These values correspond with gram-equivalents, that is, combination with eight grams of oxygen, and are expressed in kilogram-calories. The typical oxide is always meant. The figures rest chiefly upon the recent work of Rengade, de Forcrand, and Guntz. References to most of the papers are to be found in Abegg's "*Handbuch der anorganischen Chemie.*" The work of Guntz is published in *Compt. rend.*, 1903, 136, 1071; 1905, 140, 863; *Bull. Soc. chim.*, 1906, [iii], 35, 503. The work on lanthanum was done by Matignon, *Ann. Chim. Phys.*, 1906, [viii], 8, 426. The heat of oxidation of beryllium is not accurately known, but since the oxide may be decomposed by magnesium at high temperatures, the value is very probably less than 70 calories per gram-equivalent.

and neon all have very low melting points. At each recurrence of these groups with higher atomic weights the melting point rises, whereas with each recurrence of the immediately following alkali metals the melting point falls. By the time antimony is reached, this analogue of nitrogen has a melting point as high as 900° absolute, whereas the next alkali metal has the lowest melting point of all these metals. Clearly the property of melting has shifted toward the right. Other examples of a similar kind have been pointed out by others, for example, the well-known displacement from strict periodicity of argon, cobalt, and tellurium all point to an unequal rate of progression in isolated cases. Thus, this phenomenon seems to be a general one; the various properties of material seem to oscillate with varying rhythms as the atomic weights increase. The variation is so great that one may almost suspect, not only varying rhythms, but also rhythms represented by different types of mathematical functions.

These facts suggest a possible reason for the great irregularity of the last part of the periodic table. May it not be that the nature of the elements is determined by several fundamental tendencies which may be compared to the Mendelian characters of the modern theory of heredity? If these characters recur at different intervals as the atomic weight increases, a given rhythm occurring at first would necessarily be obliterated toward the end of the system. To change the analogy and borrow a term from the nomenclature of light, we may say that the tendencies, which produce the curves in this diagram, might first reinforce and afterwards interfere with one another, because they possess different wave-lengths. At first, overlapping might accentuate one set of properties; later the changing relation might annihilate this set of properties, and cause another. Thus, all the varieties of material may be functions of some few fundamental characteristics which progress at different rates as the atomic weights increase.

Any attempt to discover the nature of these fundamental tendencies must be of a highly speculative character. In our ignorance we cannot distinguish between cause and effect. The well-known definite relations of the spectrum lines suggest that at least one of the essential requirements for the existence of an atom may be susceptibility to certain definite harmonic vibrations; those compressible atoms capable of vibrating in certain rhythms may be permanent, whilst other aggregations may be unstable. The gap in the periodic system where *eka*iodine and *ekac*esium should be, and the amazing instability of the elements immediately following, supports the notion.

But here we have a cosmic puzzle for future solution. To-day we

lack adequate data, we are blocked at every turn by our ignorance; therefore, the immediate problem is to discover and test each step as carefully as possible. When the facts have been ascertained, man will have a solid basis upon which to build his future superstructure of theoretical interpretation.

The quest is not dictated by mere curiosity alone. All organic life is actuated by chemical energy, and exists in a mechanism and environment composed of chemical substances; and the effort to understand these essential conditions of human existence constitutes one of the most important objects of human endeavour. Superficial observation of the complex phenomena of life can do but little; as Faraday well knew, patient study of the fundamental laws of the physical universe alone can help to unravel the interwoven threads. Health, well-being, and a profound philosophic outlook are alike dependent upon the result. No one can predict how far we shall be enabled by means of our limited intelligence to penetrate into the mysteries of a universe immeasurably vast and wonderful; nevertheless, each step in advance is certain to bring new blessing to humanity and new inspiration to greater endeavour.

CXXX.—*Properties of Binary Mixtures of Some Liquefied Gases.*

By LANCELOT SALISBURY BAGSTER (Victorian Government Research Scholar).

IN a previous paper (Trans., 1910, **97**, 2607) an account was given by the author, in conjunction with Dr. B. D. Steele, of the vapour pressure-concentration curves of binary mixtures of liquid hydrogen sulphide with liquid hydrogen bromide and with liquid hydrogen iodide. The hydrogen bromide curve showed a mixture of minimum vapour pressure, whilst the hydrogen iodide "curve" was a straight line.

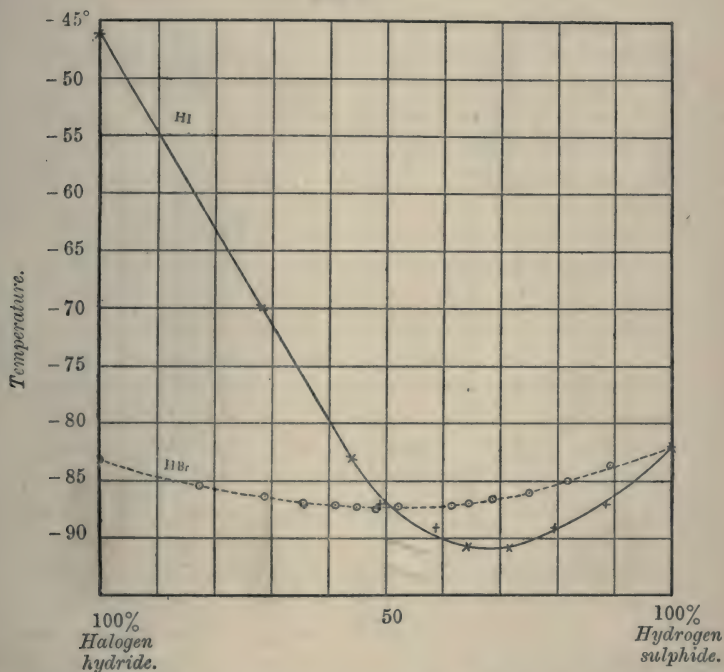
It was pointed out that such a minimum was regarded as evidence for ionisation or combination or association, and that existing evidence was against the occurrence of ionisation or association in the case of the hydrogen bromide mixtures, whilst there was no other reason than the vapour pressure curve for assuming compound formation.

As hydrogen bromide and iodide usually show a general similarity in behaviour, it was considered of interest to examine further

these mixtures. The shape of the freezing-point curve of a binary mixture being usually regarded as trustworthy evidence for or against combination, an examination of these curves was undertaken.

The curves obtained are shown in Fig. 1. It will be seen that both are of the same general type, and that neither is of the characteristic shape with two eutectic points and a maximum, exhibited by a mixture in which compound formation is taking place. There is no eutectic point in either curve, both being continuous and of the form produced by a system in which the

FIG. 1.

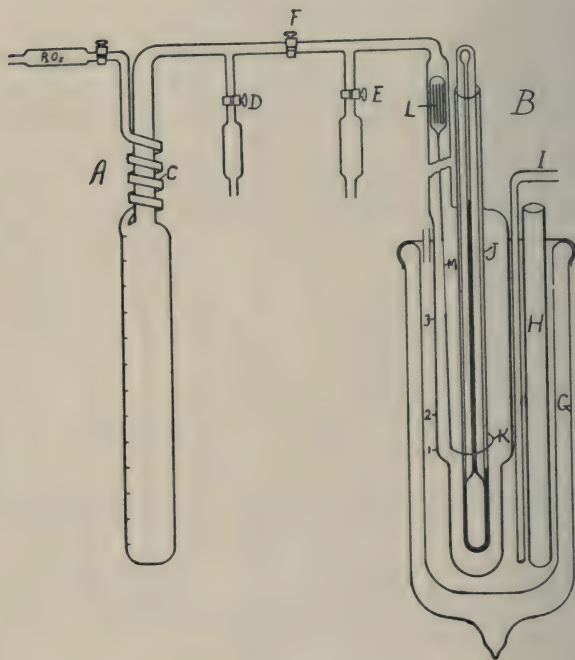


solid phase consists of mixed crystals. It will be seen that hydrogen iodide has a much greater depressing effect on the freezing point of hydrogen sulphide than has an equivalent amount of hydrogen bromide.

Tsakalotos (*Zeitsch. physikal. Chem.*, 1910, **71**, 667) concludes from the evidence of freezing-point curves and viscosity measurements that a minimum in the vapour-pressure curve of a binary mixture does not necessarily indicate the formation of compounds. Apparently the hydrogen bromide system may be regarded as adducing further evidence for this conclusion.

The apparatus used for the measurements is shown in Fig. 2. It consists of two parts, a burette *A* for measuring the liquids, the mixtures being made up by volume; and the actual freezing-point apparatus *B*. It was constructed wholly of glass, all joints being sealed together, and was so designed that a vacuum could be maintained, in order that, having once removed air, liquid could be quickly distilled from one vessel to the other without loss. All points where moisture could gain entrance were protected by

FIG. 2.



phosphoric oxide tubes. Taps were lubricated with a mixture of paraffins.

To perform an experiment, the burette *A* was immersed in a suitable refrigerant contained in a long narrow Dewar flask, and a little over 5 c.c. of one liquid, say, hydrogen sulphide, distilled in through the spiral *C*, which acted as a condenser, uncondensed gases passing out at *D*. Air was then removed by alternately exhausting at *E* with a water-pump, and admitting vapour through the tap *F*. The tube *B* was then immersed in an unsilvered Dewar flask *G*, containing light petroleum, the top of the flask being closed by a piece of sheet rubber with holes cut to admit the various

tubes, this being found to be practically air-tight and more convenient than a rubber cork when there is no great difference of pressure on the two sides. Liquid air was now blown into the tube *H*, where it boiled off, cooling the light petroleum in so doing. The petroleum bath was stirred by a current of dry air blown through the tube *I*. When the temperature, as indicated by a normal pentane thermometer contained in the tube *J*, had fallen sufficiently, an exactly measured volume of the liquid (about 5 c.c.) was distilled from *A* to *B*. The thermometer used was graduated in degrees to -200° . The column was only partly immersed, giving rise to a considerable immersion error. No attempt was made to correct the readings for this, attention being concentrated on an endeavour to keep it constant. The space between the thermometer bulb and the tube *J* was filled with petroleum, as shown by the black shading in the diagram, to ensure good thermal contact. The lower portion of the freezing-point tube was made narrow in order that the thermometer bulb should be well immersed with a small volume of liquid. Five c.c. filled it to about the point 1; the rest of the tube was wider, a further 5 c.c. changing the level only to about 2. This was to ensure as small a change as possible in the immersion error of the thermometer. For the same reason the apparatus was immersed in the petroleum bath to the point 3, well above 2, and the petroleum kept at constant level.

Having distilled 5 c.c. of hydrogen sulphide into *B*, *A* was cleaned out, about 11 c.c. of halogen hydride distilled in, and air removed by exhausting at *D* with a water pump. Having obtained the freezing point of the hydrogen sulphide, halogen hydride was distilled into *B* in small, measured quantities, the freezing point of each mixture being determined. The temperature of the bath surrounding *B* was kept well below the boiling point of the liquid in *A* when distilling, to prevent back diffusion from *B*. The solutions were mixed by means of the glass stirrer *K*, which was worked by a magnet acting on a bundle of iron wire sealed into the tube *L*. The glass stem of the stirrer was broken at *M*, and a piece of platinum wire inserted for the sake of flexibility. In order to obtain a freezing point, liquid air was blown into *H* in small quantities, keeping the bath well stirred by the air current through *I*, and the solution with the magnetic stirrer. The temperature was made to fall very slowly until crystallisation began. If much solid separated, the reading was considered doubtful. Having obtained a reading, the solid was allowed to melt, and the freezing repeated. When a total quantity of 5 c.c. of the second liquid (halogen hydride) had been added, the liquid was distilled out from *B*, and 5 c.c. of halogen hydride distilled in, its freezing

point being then determined. Finally, the burette *A* was emptied, and 5 c.c. of hydrogen sulphide were condensed in it. The curve was then begun from the halogen hydride end, finishing with the final mixture of the first series. This method was found to be the quickest and most economical for obtaining the entire range of concentrations.

The methods adopted for the preparation and purification of the liquids were similar to those described in the previous paper, except that hydrogen bromide was prepared by heating potassium bromide with phosphoric acid solution which had been concentrated to a thick syrup. Hydrogen sulphide and bromide were condensed by a mixture of solid carbon dioxide and ether, and measured at the temperature of that mixture, taken as -80° . Hydrogen iodide was condensed and measured in liquid ammonia kept at -45° by blowing a current of air through it. The change in the volume of the burette *A* due to the temperature change from -45° to -80° was neglected. For the calculation of the molecular compositions of the mixtures, densities were taken from a paper by Steele, McIntosh, and Archibald (*Phil. Trans.*, 1905, *A*, 205, 99). Knowing the relative volumes of both constituents of a mixture and the densities, it was easy to calculate the relative weights, and from these and the atomic weights the molecular percentage of each constituent was calculated. In the tables concentrations are expressed as percentage of molecules of halogen hydride.

Tables I and II give the experimental data for hydrogen bromide mixtures, table III for hydrogen iodide.

TABLE I.

Hydrogen Bromide—Hydrogen Sulphide. First Experiment.

Molecular percentage of HBr.	Freezing point.	Molecular percentage of HBr.	Freezing point.	Molecular percentage of HBr.	Freezing point.
0.0	-82°	38.6	-87.1°	55.0	-87.3°
10.7	-83.5	42.0	-87.9^{*}	58.5	-87.2
18.2	-85.0	45.5	-88.0^{*}	64.4	-86.9
25.0	-86.0	48.5	-88.0^{*}	71.2	-86.2
31.0	-86.7	48.0	-87.3	82.4	-85.3
35.7	-87.0	51.5	-87.5	100.0	-83.1

All the points in table I lie on a smooth curve, except the three marked with an asterisk at 42, 45.5, and 48.5 per cent. hydrogen bromide, which lie on a line nearly a degree too low. These readings were taken after about eighteen hours' almost continuous work. The method of reading the thermometer depended partly on the nearest ten mark; in the present case, -90° was just invisible; consequently an error in reading the thermometer was suspected.

This was to some extent confirmed by the value at 48 per cent. hydrogen bromide obtained at the end of the second half of the experiment, which should have almost corresponded with the value for 48.5 per cent. in the first set. A fresh experiment was undertaken, the curve being carefully repeated from 35 to 55 per cent. hydrogen bromide. The results are given in table II. All the points lie on a smooth curve, which, however, is about 0.2° higher than for the first experiment. As the apparatus had been cut to pieces and cleaned between the two experiments, the exact conditions may not have been recovered, with consequent small change in the thermometer error.

The curve has been drawn from the data contained in table I, rejecting the three doubtful readings. It is shown in Fig. 1.

TABLE II.

Hydrogen Bromide—Hydrogen Sulphide. Second Experiment.

Molecular percentage of HBr.	Freezing point.	Molecular percentage of HBr.	Freezing point.	Molecular percentage of HBr.	Freezing point.
35.0	-87.0°	44.2	-87.0°	55.5	-86.7°
39.8	-87.0	49.0	-87.0	100.0	-83.0
		52.5	-86.9		

Table III contains the data for hydrogen iodide. The curve is shown in Fig. 1.

TABLE III.

Hydrogen Iodide—Hydrogen Sulphide.

Molecular percentage of HI.	Freezing point.	Molecular percentage of HI.	Freezing point.	Molecular percentage of HI.	Freezing point.
0.0	-82.0°	28.4	-90.8°	56.0	-83.0°
11.3	-87.0	35.6	-90.7	71.8	-70.0
20.3	-89.0	41.0	-89.0	100.0	-46.0
		51.0	-87.0		

The author wishes to acknowledge indebtedness to Professor Masson for kind advice and for the interest he has taken in the work.

UNIVERSITY OF MELBOURNE.

CXXXI.—*The Second and Third Dissociation Constants of Orthophosphoric Acid.*

By EDMUND BRYDGES RUDHALL PRIDEAUX.

AMONG the standards of acidity (or alkalinity) used in physiological and analytical chemistry, those possessing a "balanced hydrogen ion concentration" have a particular importance in the range of concentrations from $[H]=1 \times 10^{-4}$ to $[OH]=1 \times 10^{-4}$. It was suggested to me by Professor Donnan that additional work was desirable in the case of the most important of such solutions, the alkaline phosphates. In order to bring out the points to be tested, a brief account is necessary of the methods and results of Friedenthal (*Zeitsch. Elektrochem.*, 1904, **10**, 113) and Salm (*Zeitsch. physikal. Chem.*, 1907, **57**, 492), to whose careful and pioneering work we owe the chief advance that has been made in the study of these solutions.

The salts used were Kahlbaum's purest preparations of sodium dihydrogen phosphate, disodium hydrogen phosphate, and trisodium phosphate. The hydrogen ion concentrations of solutions ($N/10$) made from these crystalline salts were determined by means of the platinum hydrogen electrode, the standards of acidity being 0.0104 and 0.001 N -hydrochloric acid. Diffusion potentials were eliminated by making all solutions decinormal with respect to sodium chloride.

The differences of method in the present work will be sufficiently apparent from what follows.

The general trustworthiness of the cells, electrodes, and methods of measurement was tested by determining the *E.M.F.* of the hydrogen electrode in various concentrations of hydrochloric acid against the N - and $N/10$ -hydrochloric acid calomel electrode, using saturated ammonium nitrate solution (Abegg and Cumming, *Trans. Faraday Soc.*, 1906–1907, **2**, 213) to eliminate diffusion potential. The results were satisfactory, and from them the single potentials of hydrogen-platinum against the 0.1 and 0.01 N -hydrochloric acid used throughout were calculated. The values 0.217 and 0.161 agree with the results of Smale (*Zeitsch. physikal. Chem.*, 1894, **14**, 577), Wilsmore (*ibid.*, 1900, **35**, 302), Sauer (*ibid.*, 1904, **47**, 170), and others.

A series of experiments was carried out to test the relative efficacy of the eliminators of diffusion potential (1) saturated potassium chloride, (2) saturated ammonium nitrate, (3) $N/10$ -sodium chloride, dissolved in, as well as connecting, the electrode solutions. All three gave the same results with 0.01 N -hydro-

chloric acid and the phosphate solutions, with the exception of those on the alkaline side of the neutral point to which it is known; (2) is not applicable. The degree of confidence to be attached to such measurements in highly hydrolysed phosphate solutions was tested in the extreme case (trisodium phosphate). The hydroxyl concentration of $N/10$ -trisodium orthophosphate is about the same as that of $N/100$ -sodium hydroxide. The electromotive force of the hydrogen electrode in alkali of this concentration against that in $N/100$ -hydrochloric acid, the two solutions being connected by saturated potassium chloride, was found to be 0.583 volt, that calculated for a 95 per cent. dissociation of the alkali being 0.589 volt. The slightly low value is due to the solvent effect of the alkali on the glass. A cell of borosilicate glass was substituted for the alkaline phosphate measurements.

The Phosphate Solutions.—The phosphoric acid was Merck's purest (D 1.73), free from nitrate, chloride, and sulphate. It was also proved to be free from metaphosphoric acid by the egg-albumin test. This point was further investigated by making up solutions of identical phosphorus and sodium content from boiled and unboiled acid. No difference in hydrogen ion concentration was detected. The strong acid was found to contain 64.4 per cent. of phosphoric oxide. From it a normal acid was made, and separately analysed. It contained 0.0682 gram of phosphoric oxide per gram.

The sodium hydroxide solution was prepared by dissolving the sticks (by alcohol) in water free from carbon dioxide. The solution (by conversion into sodium chloride) contained 0.03102 gram of sodium oxide per gram. From these standards, phosphate solutions were made by weight, having an invariable concentration of 0.1 molecule of phosphoric acid to the litre. In the case of the more alkaline solutions, the sodium hydroxide was prepared from metallic sodium.

The following table gives the result of experiments with sodium dihydrogen phosphate made as described from sodium hydroxide and phosphoric acid. The second column refers to the nature of the eliminator of diffusion potential.

TABLE I.

Normality of HCl.	Connexion.	[H]:
0.0104	0.1NaCl	1.4×10^{-4}
0.0104	0.2NaCl	1.2×10^{-4}
0.001	0.1NaCl	1.1×10^{-4}
0.10	NH_4NO_3	2.2×10^{-4}
0.10	KCl	2.0×10^{-4}

In table II the column headed "ratio" gives the number of milligram-molecules of sodium hydroxide to 10 of phosphoric acid,

and therefore the number of c.c. of the *N*-alkali to be added to 10 c.c. of the *N*-acid and made up to 100. The standard of hydrogen ion concentration was 0.01*N*-hydrochloric acid through-out, and the connecting solution saturated potassium chloride. The first sample of disodium hydrogen phosphate was made from the stock alkali and acid, the second from the salt which had been recrystallised from a neutral solution and checked by analysis as $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Mg}_2\text{P}_2\text{O}_7$.

TABLE II.

	Ratio.	[H].		Ratio.	[H].
	11.05	1.7×10^{-6}		20.5	5.9×10^{-11}
	14.45	2.6×10^{-7}		21.0	2.5×10^{-11}
	15.50	2.0×10^{-7}		21.6	2.0×10^{-11}
	16.55	1.3×10^{-7}		21.9	1.3×10^{-11}
	17.60	7.6×10^{-8}		22.2	1.2×10^{-11}
(synthetic	19.97	3.5×10^{-9}		25.0	2.9×10^{-12}
salt)	20.00	1.5×10^{-9}		30.0	6.8×10^{-13}

TABLE III.

The Results of Salm.

	Ratio.	[H].		Ratio.	[H].
(NaH_2PO_4)	10.0	9.3×10^{-5}	(Na_2HPO_4)	20.0	1.3×10^{-9}
	11.5	9.7×10^{-7}		20.3	9.8×10^{-11}
	15.5	1.5×10^{-7}		21.4	1.3×10^{-11}
	19.5	1.0×10^{-8}		30.0	4.3×10^{-13}

The high value of [H] for synthetic disodium hydrogen phosphate is probably due to the presence of a small amount of carbonate in the alkali. The irregularities in this part of the $\log[\text{H}]$ and concentration $\text{NaOH}/\text{H}_3\text{PO}_4$ curve are chiefly due to concentration errors, those in the predominating flat part to errors in measurement of electromotive force.

If the hydrogen ion concentration of these solutions is controlled by the second and third dissociation constant of orthophosphoric acid, then the above results should be capable of being expressed by one equation containing [H], [NaOH], $[\text{H}_3\text{PO}_4]$, k_2 , k_3 (the square brackets denoting concentrations). Obviously k_2 and k_3 , if unknown, could be calculated, and the calculation has a special interest, since the constants have been already determined by Abbott and Bray (*J. Amer. Chem. Soc.*, 1909, **31**, 730), using an entirely different method, namely, that of conductivity combined with the distribution ratio of ammonia between chloroform and solutions of sodium ammonium phosphates. Their results were as follows:

$$k_2 = \frac{\text{H}^+ \times \text{HPO}_4''}{\text{H}_2\text{PO}_4'} = 1.95 \times 10^{-7}.$$

$$k_3 = \frac{\text{H}^+ \times \text{PO}_4'''}{\text{HPO}_4''} = 3.6 \times 10^{-13}.$$

The constants refer to a total concentration of 0.026 gram-molecule per litre. At $C=0.1$ they will be somewhat greater. The degrees of dissociation of the salts which will be used for subsequent calculations were found to be at a total molecular concentration of 0.1— NaH_2PO_4 , 77 per cent., Na_2HPO_4 , 60 per cent. The dissociation of sodium orthophosphate was assumed the same as that of sodium pyrophosphate, $\text{Na}_3\text{HP}_2\text{O}_7$, and may be taken in round numbers as 50 per cent.

In the case of sodium dihydrogen phosphate, the calculation of $[\text{H}]$ from these data is simple, since k_3 does not enter, and the HPO_4'' produced may be taken as all derived from the original $\text{H}_2\text{PO}_4''$ produced by the primary salt dissociation. If this is represented by α_1 :

$$[\text{H}]^2 = k_2 \alpha_1 c = 2.0 \times 0.077 \times 10^{-7},$$

$$\text{and } [\text{H}] = 1.2 \times 10^{-4},$$

in good agreement with the directly observed value.

In the case of disodium hydrogen phosphate, however, the above values of k_2 and k_3 would lead to $[\text{H}] = 1 \times 10^{-10}$, instead of 1×10^{-9} . Thus, disodium hydrogen phosphate being hydrolysed to 0.055 per cent.:

$$\text{OH} = 0.1 \times 0.055 \times 0.9 = 0.045,$$

$$\text{H} = \frac{0.54 \times 10^{-14}}{0.5 \times 10^{-4}} = 1.1 \times 10^{-10}.$$

The discrepancy becomes still more apparent at lower hydrogen ion concentrations (see diagram). Its magnitude could best be determined by a recalculation of k_3 from the whole series of experimental values, since no one value is sufficiently accurate to be satisfactory from this point of view. The complete equation connecting H , α , k , c is rather cumbersome, and it has been replaced within a certain range by a simpler form. It will be seen that the latter is theoretically applicable to solutions in which the hydrogen and hydroxyl ion concentration are vanishingly small compared with the total available salt, that is, to solutions not too far from the neutral point. With this reservation, however, such an equation should prove useful in dealing with all similar salts of weak polybasic acids.

It has been assumed throughout that the degree of dissociation of each salt in the mixture is the same as that which it would have if present alone in the same concentration as that of the total. This has been justified by much experimental evidence (principle of Arrhenius, *Zeitsch. physikal. Chem.*, 1899, **31**, 218).

Let x_1 = total molecules of HPO_4 , $x_2 = \text{H}_2\text{PO}_4$, $x_3 = \text{PO}_4$ (as ion or

sodium salt), and $\alpha_1, \alpha_2, \alpha_3$ = degree of dissociation of Na_2HPO_4 , etc.:

$$\text{HPO}_4'' = \alpha_1 x_1, \quad \text{H}_2\text{PO}_4' = \alpha_2 x_2, \quad \text{PO}_4''' = \alpha_3 x_3 \quad . \quad . \quad (1)$$

$$\text{H} \cdot \times \text{HPO}_4'' = k_2[\text{H}_2\text{PO}_4'], \quad [\text{H}] \cdot \times [\text{PO}_4]''' = k_3[\text{HPO}_4]'' \quad . \quad . \quad (2)$$

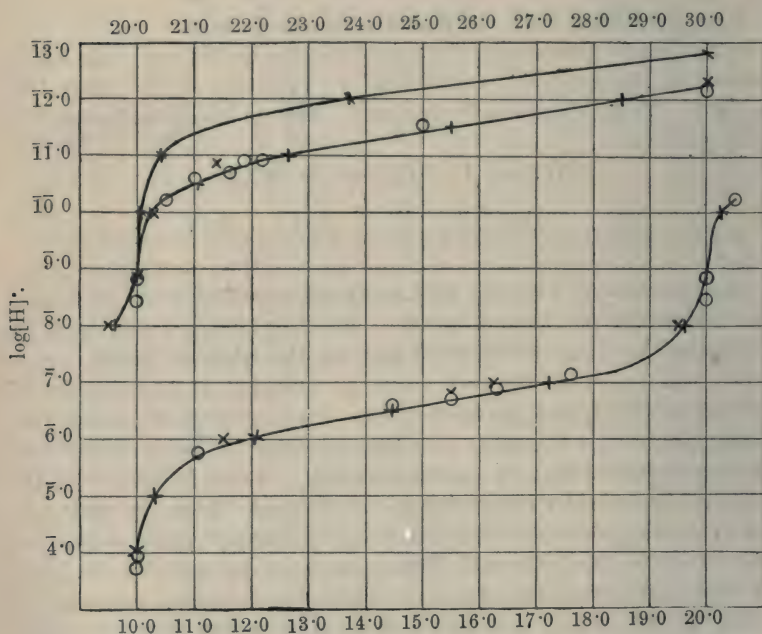
$$\text{H}_3\text{PO}_4 = x_1 + x_2 + x_3.$$

Expressing x_1 , etc., in terms of the ions from (1), and all ions in terms of $[\text{HPO}_4]''$ from (2):

$$\begin{aligned} \text{H}_3\text{PO}_4 &= \frac{\text{HPO}_4}{\alpha_1} + \frac{\text{H} \times \text{HPO}_4}{\alpha_2 k_2} + \frac{k_3 \text{HPO}_4}{\alpha_3 \text{H}} \\ &= x_1 + \frac{\alpha_1 \text{H} x_1}{\alpha_2 k_2} + \frac{\alpha_1 k_3 x_1}{\alpha_3 \text{H}}. \end{aligned}$$

Now if x_1', x_2', x_3' are the molecules of sodium hydroxide which

Upper curves: Mols. NaOH to 10 mols. H_3PO_4 .



Lower curves: Mols. NaOH to 10 mols. H_3PO_4

form total (ionised and not) disodium hydrogen phosphate, sodium dihydrogen phosphate, and trisodium phosphate:

$$\text{NaOH (total taken)} = x_1' + x_2' + x_3' + \frac{\text{OH}}{0.9}.$$

$$\text{But } x_1' = 2x_1, \quad x_2' = x_2, \quad x_3' = 3x_3.$$

$$\therefore \text{NaOH} = 2x_1 + \frac{\alpha_1 H x_1}{\alpha_2 k_2} + \frac{\alpha_1 k_3 3x_1}{\alpha_3 H},$$

$$\text{and } \frac{\text{NaOH}}{H_3\text{PO}_4} = \frac{2 + \frac{\alpha_1 H}{\alpha_2 k_2} + \frac{3\alpha_1 k_3}{\alpha_3 H} + \frac{k_w}{\alpha_4 H}}{1 + \frac{\alpha_1 H}{\alpha_2 k_2} + \frac{\alpha_1 k_3}{\alpha_3 H}}.$$

Now introducing the values* $\alpha_1 = 0.06$, $\alpha_2 = 0.077$, $\alpha_3 = 0.05$, $\alpha_4(\text{NaOH}) = 0.9$ [arrived at by Abbott and Bray from conductivity and other data (*loc. cit.*)], and $k_w = 0.54 \times 10^{-14}$, interpolated from the data for 16° :

$$\frac{\text{NaOH}}{H_3\text{PO}_4} = \frac{2 + \frac{0.78H}{k_2} + \frac{3.6k_3}{H} + \frac{0.6 \times 10^{-14}}{H}}{1 + \frac{0.78H}{k_2} + \frac{1.2k_3}{H}}.$$

Since the term containing k_3 does not at all influence the ratio until $[H]'$ becomes less than 5×10^{-8} , this equation was first used to find the most probable value of k_2 . It was found that the mean of the values obtained from the separate experimental points lay very near 2.0×10^{-7} , and this confirmation of Abbott and Bray's result allows of its adoption with considerable confidence in the subsequent calculation of k_3 . The same simplified formula was employed down to a hydrogen ion concentration of 1×10^{-11} , since it was found that at that point it still gave results agreeing with those obtained from the longer equation used for the more alkaline solutions. The latter is deduced as follows:

Let c_2 be the total concentration of sodium hydroxide in molecules per litre, and c_1 be that of the phosphoric acid ($= 0.1$ constantly). Let x_1 and x_2 be the fractions of original phosphoric acid which form total sodium dihydrogen phosphate and disodium hydrogen phosphate (ionised or not). Let α_1 , α_2 , α_3 now be the degrees of dissociation of sodium dihydrogen phosphate, disodium hydrogen phosphate, and trisodium phosphate:

$$\text{NaH}_2\text{PO}_4 = x_1 c_1, \quad \text{Na}_2\text{HPO}_4 = x_2 c_1,$$

$$\text{Na}_3\text{PO}_4 = (1 - x_1 - x_2) c_1,$$

$$\text{NaOH} = c_2 - x_1 c_1 - 2x_2 c_1 - 3(1 - x_1 - x_2) c_1,$$

$$[\text{OH}] = \alpha_4 [c_2 + c_1(2x_1 + x_2 - 3)] = \frac{0.54 \times 10^{-14}}{H} \quad . \quad . \quad . \quad (1).$$

$$\text{Also: } H \times \alpha_3 c_1 (1 - x_1 - x_2) = k_3 \alpha_2 x_2 c_1 \quad . \quad . \quad . \quad (2)$$

$$H \times \alpha_2 x_2 c_1 = k_2 \alpha_1 x_1 c_1 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

* Alterations of as much as 10 per cent. in α_1 , etc., leave the calculated values of k_2 , k_3 of the same order. Thus, taking α as 0.6 throughout, k_2 and k_3 are each increased by about half a unit.

From (3):
$$x_1 = \frac{Hx_2a_2}{k_2a_1} \dots \dots \dots (4).$$

From (2) and (4):
$$Ha_3 - Ha_3x_2 - \frac{H^2a_3a_2x_2}{k_2a_1} = k_3a_2x_2.$$

Clearing of fractions and introducing the values of a_1 , etc.:

$$x_1 = \frac{k_2H}{0.77H^2 + k_2H + 1.2k_2k_3},$$

$$x_2 = \frac{0.78H^2}{0.77H^2 + k_2H + 1.2k_2k_3}.$$

Substituting these in equation (1):

$$H^3(0.77c_2 - 0.75c_1) + H^2(k_2c_2 - 2k_2c_1 - 0.6 \times 10^{-14}) +$$

$$H(1.2k_2k_3c_2 - 3.6k_2k_3c_1 - 0.6 \times 10^{-14}k_2) - 1.2 \times 0.6 \times 10^{-14}k_2k_3 = 0,$$

and inserting the numerical values of H , c_2 and $k_2 = 2.0 \times 10^{-7}$, equations were obtained which were solved for k_3 . The mean of all values of k_3 was found to be slightly over 3.0×10^{-12} , and it is believed that this represents to the closest approximation possible at present the third dissociation constant of phosphoric acid at the stated concentration.

The constants k_2 and k_3 were then introduced into the equations, which were used for the calculation of corresponding values of $[H]$ and c_2 (+ on the diagram). The agreement of this curve with the experimental points of Salm (\times on the diagram) and the present work (\circ on the diagram) is, as will be seen by studying the units, rather better than was to be expected from the accuracy of the measurements in most cases.

On the other hand, two specimen points (\star on the diagram) at $[H] = 1 \times 10^{-10}$, 1×10^{-11} , 1×10^{-12} , and Na_3PO_4 , calculated from $k_3 = 3.6 \times 10^{-13}$, cannot by any means be reconciled with the general trend of the neutralisation curve.

The following is a list of the hydrogen ion concentrations experimentally found for the most important mixtures, compared with the values calculated from the revised constants.

NaOH to $10H_3PO_4$.	$[H]$ found.	$[H]$ calculated.
10.0 (NaH_2PO_4)	9.3×10^{-5} (S.)	1.2×10^{-4}
	$1.0 - 2.0 \times 10^{-4}$ (P.)	
17.2		1.0×10^{-7}
17.7 (neutral point at 16.0°)		0.73×10^{-7}
17.6	0.76×10^{-7}	
20.0 (Na_2HPO_4)	1.3×10^{-9} (S.)	1.0×10^{-9}
20.0 (Na_2HPO_4)	1.5×10^{-9} (P.)	
25.0 ($Na_2HPO_4 + Na_3PO_4$)	2.9×10^{-12} (P.)	4.0×10^{-12}
30.0 (Na_3PO_4)	$\begin{cases} 4.3 \times 10^{-13} \text{ (S.)} \\ 5.9 \times 10^{-13} \text{ (P.)} \end{cases}$	5.0×10^{-13}

CXXXII.—*Some Derivatives of Gelsemine.*

By CHARLES WATSON MOORE.

IN a recent communication (Trans., 1910, **97**, 2223) the author has described the isolation of the alkaloid gelsemine, in a pure state, from the rhizome and roots of *Gelsemium sempervirens*, Aiton, and has shown that it possesses the formula $C_{20}H_{22}O_2N_2$.

Apart from some of the salts of gelsemine, the only derivatives of the base that have previously been described are the methiodide and the hydrochlorides of the acetyl and benzoyl derivatives (Goeldner, *Ber. Deut. pharm. Ges.*, 1895, **5**, 330). Even these derivatives do not appear to have been obtained in a pure condition, as their analysis led Goeldner (*loc. cit.*) to the conclusion that the parent base possessed the formula $C_{22}H_{26}O_3N_2$, instead of $C_{20}H_{22}O_2N_2$, which the present author has shown to be the correct one.

A quantity of gelsemine being available, it appeared of interest to undertake an investigation of some derivatives of the alkaloid, as it was hoped that thereby some light might be thrown on its constitution. Although the amount of material at disposal did not suffice for extending our knowledge in this direction, a number of interesting derivatives have been prepared.

Attempts to obtain definite oxidation products from gelsemine were unsuccessful owing to the ease with which the alkaloid breaks down when acted on by oxidising agents. On the other hand, the base is very stable towards reducing agents, since it remains intact on boiling its alcoholic solution with sodium. A similar stability is shown towards alkali hydroxides.

On boiling gelsemine for some hours with concentrated hydrochloric acid, it has been found that three new bases are formed. The chief product of this reaction is an amorphous substance possessing the formula $C_{20}H_{24}O_3N_2$, and which corresponds, therefore, with gelsemine, to which the elements of one molecule of water have been added. It has been designated as *apogelsemine*, and several of its derivatives have been prepared. The other two bases which are formed together with *apogelsemine* possess the formulæ $C_{20}H_{23}O_2N_2Cl$ and $C_{20}H_{24}O_3N_2$ respectively, the latter being a hydrolytic product of the former. Both these bases crystallise readily, and have been designated as *chloroisoapogelsemine* and *isoapogelsemine* respectively. They and several of their derivatives have now been characterised.

It has further been observed that on heating gelsemine methiodide with potassium hydroxide, or *gelsemine methyl*

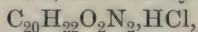
hydroxide with water, at about 200° , an anomalous change takes place, inasmuch as the expected gelsemethine is not formed, gelsemine being regenerated with the elimination of methyl alcohol.

The *methyl hydroxide* of apogelsemine behaves in an analogous manner, as on heating with water apogelsemine is regenerated.

EXPERIMENTAL.

The gelsemine employed was isolated from the dried rhizome and roots of *Gelsemium sempervirens*, Aiton, in the manner previously described (*loc. cit.*).

The alkaloid crystallises from acetone in handsome, glistening prisms, melting at 178° , and has $[\alpha]_D + 15.9^{\circ}$ in chloroform solution. As already mentioned, it possesses the empirical formula $C_{20}H_{22}O_2N_2$. It is monobasic, and its hydrochloride,



forms small, glistening prisms, melting at about 300° , and having $[\alpha]_D + 2.6^{\circ}$ in aqueous solution.

Gelsemine is not attacked by even prolonged heating with potassium hydroxide solution or by treatment with sodium in boiling alcoholic solution. On the other hand, it is very readily oxidised by potassium permanganate, but no definite products have been obtained by this means. The alkaloid contains no methoxyl or ethoxyl group.

Acetylgelsemine, $C_{20}H_{21}ON_2 \cdot OAc$.—The presence of a hydroxyl group in gelsemine has already been shown by Goeldner (*loc. cit.*), who obtained the acetyl and benzoyl derivatives of the base in the form of their hydrochlorides. The acetylated base, however, has not previously been described.

A quantity (5 grams) of gelsemine was boiled for one hour with acetic anhydride (50 grams) in the presence of a trace of pyridine. The reaction mixture was then shaken with ice and water until a homogeneous liquid was obtained, after which the base was precipitated by sodium carbonate and extracted with ether.

Acetylgelsemine crystallises from methyl alcohol in large, colourless prisms, containing one molecule of the solvent, which melt indefinitely at 60 — 70° . The methyl alcohol of crystallisation is partly lost by exposure to the air, and completely on heating at 100° , after which the base melts at 106 — 108° :

0.3760,* when heated at 100° , lost 0.0295 CH_4O . $CH_4O = 7.8$.

0.1256 † gave 0.3333 CO_2 and 0.0760 H_2O . $C = 72.4$; $H = 6.7$.

0.1304 † „ 0.3460 CO_2 „ 0.0778 H_2O . $C = 72.3$; $H = 6.7$.

$C_{22}H_{24}O_3N_2 \cdot CH_4O$ requires $CH_4O = 8.1$ per cent.

$C_{22}H_{24}O_3N_2$ requires $C = 72.5$; $H = 6.6$ per cent.

* Air-dried.

† Dried at 120° .

0.3490,† made up to 20 c.c. with chloroform, gave $\alpha_D + 0^\circ 50'$ in a 2-dcm. tube, whence $[\alpha]_D + 23.9^\circ$.

Acetylgelsemine hydrochloride, $C_{20}H_{21}ON_2 \cdot OAc, HCl$, was prepared by passing dry hydrogen chloride into an ethereal solution of the base. It crystallises readily, in small prisms, from a mixture of methyl alcohol and ethyl acetate:

0.1346 gave 0.0510 $AgCl$. $Cl = 9.3$.

$C_{22}H_{24}O_3N_2, HCl$ requires $Cl = 8.8$ per cent.

Gelsemine Methiodide, $C_{20}H_{22}O_2N_2 \cdot CH_3I$.—This substance was first prepared by Goeldner (*loc. cit.*), but it was not correctly characterised by him. It crystallises from alcohol in large, handsome prisms, and from water in glistening leaflets containing one molecule of water of crystallisation:

0.6006,* when heated at 120° , lost 0.0210 H_2O . $H_2O = 3.5$.

0.1632 † gave 0.3250 CO_2 and 0.0790 H_2O . $C = 54.3$; $H = 5.4$.

0.2820 † „ 0.1420 AgI . $I = 27.2$.

$C_{21}H_{25}O_2N_2I, H_2O$ requires $H_2O = 3.7$ per cent.

$C_{21}H_{25}O_2N_2I$ requires $C = 54.3$; $H = 5.4$; $I = 27.4$ per cent.

0.2050,† made up to 20 c.c. with water, gave $\alpha_D + 0^\circ 11'$ in a 2-dcm. tube, whence $[\alpha]_D + 8.9^\circ$.

With the object of obtaining the corresponding gelsemethine, a quantity (1 gram) of gelsemine methiodide was heated at 200° for some hours with about 25 c.c. of 20 per cent. aqueous potassium hydroxide. When cool, the alkaline liquid was acidified, filtered, rendered alkaline with sodium carbonate, and extracted with ether. A quantity of a substance was thus removed, which, after crystallisation from acetone, formed glistening prisms, melting at 178° , and was found to be gelsemine.

It is thus seen that gelsemine methiodide behaves in an anomalous manner on heating with potassium hydroxide, inasmuch as it does not yield the expected gelsemethine, but is deprived of methyl alcohol, the original base being regenerated.

For the preparation of *gelsemine methyl hydroxide*, the corresponding methiodide was treated with silver sulphate, and to the resulting methosulphate the requisite amount of barium hydroxide was added. After removing the barium sulphate, the strongly alkaline aqueous solution of the quaternary hydroxide was concentrated to the consistency of a syrup, but all attempts to isolate the methyl hydroxide in a crystalline condition were unsuccessful.

On heating an aqueous solution of gelsemine methyl hydroxide at 220 – 240° , the base was found to undergo a change analogous to that shown above to occur when the corresponding methiodide

* Air-dried.

† Dried at 120° .

is heated with aqueous potassium hydroxide, methyl alcohol being eliminated, with the regeneration of gelsemine.

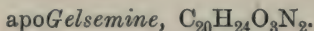
The Action of Hydrochloric Acid on Gelsemine.

Since alkali hydroxides and reducing agents had no action on gelsemine, the effect of heating the base with acids was investigated.

A quantity (10 grams) of gelsemine was boiled for about three hours with 100 c.c. of concentrated hydrochloric acid. The solution was then evaporated to dryness under diminished pressure, the last traces of water being removed by repeated evaporation with alcohol. The product was dissolved in a small quantity of boiling absolute alcohol, and boiling ethyl acetate was added to the solution until a slight turbidity was produced. On keeping, a crystalline product separated, which was collected, washed with ethyl acetate, and dried, when it amounted to between 8 and 9 grams. The product contained in the filtrate from the hydrochlorides could not be readily crystallised, and is referred to later.

The above-mentioned crystalline substance appeared homogeneous, and, on analysis, gave numbers corresponding with the formula $C_{20}H_{26}O_4N_2 \cdot HCl$, but on attempting to prepare the corresponding base, it was found to consist of a mixture of the hydrochlorides of three bases, which were separated as follows.

Five grams of the above-mentioned mixed hydrochlorides were dissolved in about 250 c.c. of 30 per cent. alcohol, and 0.7 gram of sodium carbonate, dissolved in water, was added to the hot solution. A current of steam was then passed through the mixture until all the alcohol was removed, when a crystalline substance separated. This was removed from the hot solution, and washed with a little boiling water, when it formed small, glistening prisms, in amounts varying from 0.5 to 0.8 gram.



The aqueous liquid from which the above-mentioned crystalline substance had been separated was extracted with chloroform, which removed a quantity of an amorphous base soluble in water. This was dissolved in a small quantity of acetone, and on inoculating the solution with *isoapogelsemine*, subsequently described, about 0.3 gram of the latter slowly separated.

The acetone solution from which the crystalline substance had been removed yielded about 3 grams of a base: this represents the chief product of the action of hydrochloric acid on gelsemine, and although the substance is amorphous, it was found to be homogeneous, and has been designated as *apogelsemine*.

apoGelsemine is a strongly basic substance, readily soluble in

hot water and most organic solvents with the exception of ether, in which it is only sparingly soluble. All attempts to obtain the base in a crystalline condition were unsuccessful.

apoGelsemine Hydrochloride, $C_{20}H_{24}O_3N_2 \cdot HCl \cdot H_2O$.—This salt was prepared by evaporating an aqueous solution of *apogelsemine* in dilute hydrochloric acid to dryness, and crystallising the residue from a mixture of alcohol and ethyl acetate. It forms colourless, glistening needles, melting indefinitely between 250° and 260° . After drying at 115 – 120° it was analysed:

0.1805 gave 0.0660 AgCl. Cl = 9.0.

0.1432 „ 0.3176 CO_2 and 0.0919 H_2O . C = 60.5; H = 7.1.

0.1440 „ 0.3204 CO_2 „ 0.0920 H_2O . C = 60.6; H = 7.1.

0.2292 „ 14.0 c.c. N_2 at 26° and 770 mm. N = 6.9.

$C_{20}H_{26}O_4N_2 \cdot HCl$ requires C = 60.8; H = 6.8; N = 7.1;

Cl = 9.0 per cent.

From these figures *apogelsemine* would appear to have the formula $C_{20}H_{26}O_4N_2$, yielding the hydrochloride $C_{20}H_{26}O_4N_2 \cdot HCl$. It was found, however, from the analysis of the methiodide and the acetyl derivatives that the formula of the base is $C_{20}H_{24}O_3N_2$, the hydrochloride crystallising with one molecule of water, which is not lost on drying at 120° . Thus *apogelsemine* appears to be formed by the addition of the elements of one molecule of water to gelsemine.

A determination of the specific rotatory power of the hydrochloride gave the following result:

0.4142, made up to 20 c.c. with water, gave $\alpha_D + 0^\circ 47'$ in a 2-dcm. tube, whence $[\alpha]_D + 18.9^\circ$.

apoGelsemine Methiodide, $C_{20}H_{24}O_3N_2 \cdot CH_3I$.—This derivative was prepared by the action of methyl iodide on a solution of *apogelsemine* in ethyl acetate. It crystallises in colourless prisms, melting and decomposing at about 295° :

0.1272 gave 0.2456 CO_2 and 0.0660 H_2O . C = 52.6; H = 5.7.

$C_{21}H_{27}O_3N_2I$ requires C = 52.3; H = 5.6 per cent.

0.2670, made up to 20 c.c. with water, gave $\alpha_D + 0^\circ 20'$ in a 2-dcm. tube, whence $[\alpha]_D + 12.4^\circ$.

apoGelsemine methyl hydroxide was prepared in the manner described in connexion with gelsemine methyl hydroxide, but, like that substance, it could not be obtained in a crystalline condition.

With the endeavour to obtain the corresponding *apogelsemethine*, a quantity of *apogelsemine* methyl hydroxide was heated in aqueous solution for three hours at 210° . The liquid was then acidified, filtered, and the filtrate rendered alkaline with sodium carbonate, and extracted with chloroform. This removed a quantity of an amorphous base, which was found to be *apogelsemine*, since on

warming with methyl iodide it was converted into *apogelsemine* methiodide. (Found, C=52.5; H=6.0. Calc., C=52.3; H=5.6 per cent.) *apoGelsemine* methyl hydroxide behaves, therefore, in the same anomalous manner as *gelsemine* methyl hydroxide, inasmuch as by the above treatment methyl alcohol is eliminated and *apogelsemine* regenerated.

Diacetylalogelsemine Hydrochloride, $C_{20}H_{22}ON_2(OAc)_2 \cdot HCl$.—The presence of two hydroxyl groups in *apogelsemine* was shown by the formation of a diacetyl derivative. *apoGelsemine* (2 grams) was boiled for about two hours with acetic anhydride (25 grams) in the presence of a trace of pyridine. The solution was afterwards evaporated almost to dryness under diminished pressure, the residue dissolved in ether, and dry hydrogen chloride passed into the solution. A white precipitate was produced, which was collected, dried in a desiccator, and crystallised from absolute alcohol, when it was obtained in glistening plates, melting at 286° :

0.3154 gave 0.0940 AgCl. Cl=7.4.

0.1384 „ 0.3150 CO_2 and 0.0815 H_2O . C=62.1; H=6.5.

$C_{24}H_{29}O_5N_2Cl$ requires C=62.5; H=6.3; Cl=7.7 per cent.

This substance is thus identified as the *hydrochloride* of *diacetylalogelsemine*. A determination of its specific rotatory power gave the following result:

0.2150, made up to 20 c.c. with water, gave $\alpha_D + 0^{\circ}28'$ in a 2-dcm. tube, whence $[\alpha]_D + 21.7^{\circ}$.

Diacetylalogelsemine was obtained from the hydrochloride, but it could not be crystallised.

Monoacetylalogelsemine, $C_{20}H_{23}O_2N_2 \cdot OAc$.—On boiling an aqueous alcoholic solution of *diacetylalogelsemine* with potassium carbonate for a few minutes, one acetyl group is removed with the formation of the monoacetyl derivative.

Monoacetylalogelsemine crystallises from methyl alcohol in small, glistening prisms, which melt at 295 — 298° . The substance appears to crystallise with one molecule of methyl alcohol, but this is so readily lost on exposure to the air that an exact determination of its amount was not practicable:

0.1444 * gave 0.3660 CO_2 and 0.0900 H_2O . C=69.1; H=6.9.

$C_{22}H_{26}O_4N_2$ requires C=69.1; H=6.8 per cent.

Chloroisoapogelsemine, $C_{20}H_{23}O_2N_2Cl$.

As above mentioned, during the separation of the bases from the mixed hydrochlorides obtained by the action of hydrochloric acid on *gelsemine*, a small quantity (0.5 to 0.8 gram) of a substance

* Dried at 120° .

was isolated, which differed from *apogelsemine* by its insolubility in hot water.

This substance crystallises from dilute alcohol or ethyl acetate in glistening prisms. It begins to decompose at about 220° , but shows no definite melting point:

0.1304 gave 0.3230 CO_2 and 0.0800 H_2O . $\text{C}=67.5$; $\text{H}=6.8$.

0.1382 „ 0.3416 CO_2 „ 0.0836 H_2O . $\text{C}=67.4$; $\text{H}=6.7$.

0.2485 „ 17.0 c.c. N_2 at 25° and 782 mm. $\text{N}=7.8$.

0.2782 „ 0.1070 AgCl . $\text{Cl}=9.5$.

$\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}_2\text{Cl}$ requires $\text{C}=67.0$; $\text{H}=6.4$; $\text{N}=7.8$; $\text{Cl}=9.9$ per cent.

This substance would thus appear to be a monochloro-derivative of *apogelsemine*, more particularly as it can be obtained by boiling *apogelsemine* with hydrochloric acid. On hydrolysis it does not, however, regenerate *apogelsemine*, but yields a crystalline isomeride of the latter. It would therefore appear probable that the chloro-derivative is not related directly to *apogelsemine*, but to the new crystalline isomeride. It is therefore proposed to designate it as *chloroisoapogelsemine*, its hydrolytic product being named *isoapogelsemine*.

A determination of its specific rotatory power gave the following result:

0.2448, made up to 20 c.c. with chloroform, gave $\alpha_D + 1^{\circ}49'$ in a 2-dm. tube, whence $[\alpha]_D + 74.2^{\circ}$.

Chloroisoapogelsemine Aurichloride, $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}_2\text{Cl} \cdot \text{HAuCl}_4 \cdot \text{H}_2\text{O}$.—This salt crystallises from dilute alcohol in orange prisms, which decompose at 160° , and appear to retain a molecule of water which is not lost at 120° :

0.1820 gave 0.0494 Au. $\text{Au}=27.1$.

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{Cl}_5\text{Au} \cdot \text{H}_2\text{O}$ requires $\text{Au}=27.5$ per cent.

Chloroisoapogelsemine Methiodide, $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}_2\text{Cl} \cdot \text{CH}_3\text{I}$.—This substance was prepared by the action of methyl iodide on an alcoholic solution of *chloroisoapogelsemine*. It crystallises from methyl alcohol in glistening prisms, melting and decomposing at about 265° :

0.1485 gave 0.2750 CO_2 and 0.0740 H_2O . $\text{C}=50.5$; $\text{H}=5.5$.

$\text{C}_{21}\text{H}_{26}\text{O}_2\text{N}_2\text{ClI}$ requires $\text{C}=50.3$; $\text{H}=5.2$ per cent.

Chloroacetylisoapogelsemine, $\text{C}_{20}\text{H}_{22}\text{ON}_2\text{Cl} \cdot \text{OAc}$.—*Chloroisoapogelsemine* was dissolved in about ten times its weight of acetic anhydride, and, after the addition of a drop of pyridine, the solution was boiled for two hours. The reaction mixture was then poured into water, the base precipitated by means of sodium carbonate, and extracted with chloroform. *Chloroacetylisoapogelsemine* crystal-

lises from methyl alcohol in small, colourless prisms, melting at 180° :

0.1340 gave 0.3234 CO_2 and $0.0770 \text{ H}_2\text{O}$. $\text{C}=65.8$; $\text{H}=6.4$.

$\text{C}_{22}\text{H}_{25}\text{O}_3\text{N}_2\text{Cl}$ requires $\text{C}=65.9$; $\text{H}=6.2$ per cent.

0.2040, made up to 20 c.c. with chloroform, gave $\alpha_D + 2^{\circ}55'$ in a 2-dcm. tube, whence $[\alpha]_D + 142.9^{\circ}$.

Action of Diethylaniline on Chloroisoapogelsemine.

If chloroisoapogelsemine be boiled with diethylaniline for a short time it loses the elements of hydrochloric acid with the formation of a base which appears to be an isomeride of gelsemine.

One gram of chloroisoapogelsemine was dissolved in 10 grams of diethylaniline, and the solution boiled for about ten minutes. Aqueous sodium carbonate was then added to the mixture, and the diethylaniline removed by distilling in a current of steam. On extracting the aqueous liquid with ether, and removing the solvent, a base was obtained which crystallised from acetone in glistening prisms, melting at $105\text{--}108^{\circ}$.

The air-dried crystals contain one molecule of acetone, which is lost on heating at 100° , the base then melting at $140\text{--}145^{\circ}$:

0.1388,* when heated at 100° , lost $0.0210 \text{ C}_3\text{H}_6\text{O}$. $\text{C}_3\text{H}_6\text{O}=15.1$.

0.1188 † gave 0.3224 CO_2 and $0.0752 \text{ H}_2\text{O}$. $\text{C}=74.0$; $\text{H}=7.0$.

$\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}_2, \text{C}_3\text{H}_6\text{O}$ requires $\text{C}_3\text{H}_6\text{O}=15.3$ per cent.

$\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}_2$ requires $\text{C}=74.5$; $\text{H}=6.8$ per cent.

0.1192, † made up to 20 c.c. with chloroform, gave $\alpha_D + 0^{\circ}18'$ in a 2-dcm. tube, whence $[\alpha]_D + 25.2^{\circ}$.

The substance is therefore isomeric with gelsemine, differing from the latter in its melting point and its specific rotatory power. The melting point, however, does not fall when the substance is mixed with gelsemine, so that it is conceivable that the preparation may be a mixture of gelsemine and an isomeride. The quantity of material available did not permit of its further examination.

Bromoisoapogelsemine, $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}_2\text{Br}$.—If gelsemine is boiled for some hours with hydrobromic acid, a small yield (15 per cent.) of a bromoisoapogelsemine is obtained, together with the above-described mixture of apo- and isoapo-gelsemine.

Bromoisoapogelsemine crystallises from ethyl acetate in glistening plates. Like the corresponding chloro-derivative, it begins to decompose at about 220° , but shows no definite melting point:

0.1268 gave 0.2790 CO_2 and $0.0676 \text{ H}_2\text{O}$. $\text{C}=60.0$; $\text{H}=5.9$.

0.1032 „ 0.0486 AgBr . $\text{Br}=20.0$.

$\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}_2\text{Br}$ requires $\text{C}=59.6$; $\text{H}=5.7$; $\text{Br}=19.8$ per cent.

* Air-dried.

† Dried at 100° .

The quantity of material available did not suffice for its further examination.

isoapoGelsemine, $C_{20}H_{24}O_3N_2$.

It has already been stated that, on crystallising the mixed hydrochlorides obtained by the action of hydrochloric acid on gelsemine, only about 80 per cent. of the product was readily obtained in a crystalline condition. The material contained in the filtrate from the crystalline hydrochlorides was therefore dissolved in water, excess of sodium carbonate added, and the base extracted with a large volume of chloroform. On concentrating the chloroform solution, a substance separated from the boiling liquid in small, colourless prisms, melting at about $290-300^\circ$. This compound was found to be identical with that obtained by the hydrolysis of chloro*isoapogelsemine*, and has been designated as *isoapogelsemine*. After recrystallisation from alcohol, the melting point became constant at about 310° :

0.1390 gave 0.3614 CO_2 and 0.0920 H_2O . $C=70.9$; $H=7.3$.

0.1408 „ 0.3641 CO_2 „ 0.0920 H_2O . $C=70.5$; $H=7.2$.

0.2432 „ 17.0 c.c. N_2 at 26° and 764 mm. $N=7.8$.

$C_{20}H_{24}O_3N_2$ requires $C=70.6$; $H=7.1$; $N=8.2$ per cent.

0.4812, made up to 20 c.c. with pyridine, gave $\alpha_D + 0^\circ 48'$ in a 2-dcm. tube, whence $[\alpha]_D + 16.6^\circ$.

isoapoGelsemine is almost insoluble in most solvents, with the exception of pyridine, in which it dissolves fairly readily.

isoapoGelsemine Hydrochloride, $C_{20}H_{24}O_3N_2 \cdot HCl \cdot H_2O$.—This salt was prepared in the same manner as *apogelsemine hydrochloride*. Like the latter, it retains one molecule of water of crystallisation, which is not lost on heating at 120° :

0.1200 gave 0.2656 CO_2 and 0.0788 H_2O . $C=60.4$; $H=7.3$.

$C_{20}H_{25}O_3N_2Cl \cdot H_2O$ requires $C=60.8$; $H=6.8$ per cent.

0.2090, made up to 20 c.c. with water, gave $\alpha_D + 0^\circ 34'$ in a 2-dcm. tube, whence $[\alpha]_D + 27.1^\circ$.

isoapoGelsemine Methiodide, $C_{20}H_{24}O_3N_2 \cdot CH_3I$.—This substance was formed by the action of methyl iodide on *isoapogelsemine* in alcoholic solution. It crystallises from methyl alcohol in glistening plates, melting and decomposing at 266° :

0.2445 gave 0.1180 AgI . $I=26.0$.

$C_{21}H_{27}O_3N_2I$ requires $I=26.3$ per cent.

A determination of its specific rotatory power gave the following result:

0.3260, made up to 20 c.c. with water, gave $\alpha_D + 0^\circ 55'$ in a 2-dcm. tube, whence $[\alpha]_D + 28.1^\circ$.

Diacetylisoapogelsemine Hydrochloride, $C_{20}H_{22}ON_2(OAc)_2 \cdot HCl$.—This derivative was prepared in the same manner as the above-described diacetyl*apogelsemine* hydrochloride. Unlike the latter compound, it is very sparingly soluble in boiling absolute alcohol, but dissolves readily in hot 95 per cent. alcohol, separating in glistening plates, which contain one molecule of water of crystallisation, and melt at 305° :

0.1460 gave 0.3236 CO_2 and 0.0870 H_2O . $C=60.4$; $H=6.6$.

0.2706 „ 0.0810 $AgCl$. $Cl=7.4$.

$C_{24}H_{29}O_5N_2Cl \cdot H_2O$ requires $C=60.2$; $H=6.4$; $Cl=7.4$ per cent.

0.2304, made up to 20 c.c. with water, gave $\alpha_D + 0^{\circ}34'$ in a 2-dm. tube, whence $[\alpha]_D + 24.6^{\circ}$.

Diacetylisoapogelsemine was prepared from its hydrochloride, but could not be crystallised. No monoacetyl derivative could be obtained from it.

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CXXXIII.—*The Constituents of the Bulb of Buphane disticha.*

By FRANK TUTIN.

Buphane disticha, Herb. (formerly known as *Boophane toxicaria*, Herb.), is a bulbous plant belonging to the *Amaryllidaceae*. It is a native of South Africa, where it is known as the "poison bulb," or, to the Dutch, as "gift-bol," and is a frequent, although nowhere abundant, object on the Veldt. The plant, which is stated to have been used as an arrow poison, and in the treatment of the disease known as red-water (Smith, *A Contribution to South African Materia Medica*, 3rd Ed., pp. 158 and 180), has long been known to possess toxic properties, but it does not appear to have been chemically examined. It has, however, been stated to contain brucine, but this has since been denied, it being affirmed that the alkaloid was aconitine (Oliver, *Chemist and Druggist*, 1908, **72**, 140).

The present investigation has shown that neither brucine nor aconitine is present in *Buphane disticha*, but that the principal alkaloid is an amorphous base, designated as *buphanine*, which resembles hyoscyne in its physiological action. At least three other alkaloids are present, one of which has been identified as narcissine

(Ewins, Trans., 1910, **97**, 2406). The unusually large amount of copper which is present in the bulb may possibly also contribute to its poisonous properties.

EXPERIMENTAL.

The material employed in this investigation consisted of the bulbs of *Buphane disticha*, Herb., which varied in weight from 140 to 500 grams, and had been specially collected in South Africa for the purpose.

The dried inner portion of the bulb was found to contain a considerable amount of an alkaloid, whereas the dead, outer layers were practically free from such a substance.* On this account, only the inner portions of the bulbs were employed for this investigation.

A quantity (3.97 kilograms) of the dried inner portions of the bulbs, representing about 54.5 kilograms of the entire fresh bulbs, were completely extracted by continuous percolation with hot alcohol. After removing the greater part of the solvent, a dark-coloured extract was obtained, which amounted to 766 grams. The whole of this was mixed with water, and steam passed through the mixture for several hours. The distillate, which contained some drops of oil, was extracted with ether. This removed about 2 grams of an essential oil containing furfuraldehyde, together with a small amount of an acid having the odour of valeric acid.

After the distillation of the extract with steam, as above described, there remained a dark-coloured aqueous liquid (A), together with a quantity of a black resin (B). These products were separated while still hot, the resin being repeatedly washed with hot water.

Examination of the Aqueous Liquid (A).

The aqueous liquid (A), on cooling, deposited a relatively small amount of a brown, amorphous product. Nothing definite could be isolated from this solid, and, on ignition, it left an appreciable proportion of residue, consisting chiefly of copper oxide.

Isolation of Acetovanillone.

The filtered aqueous liquid was then extracted six times with ether, the ethereal liquids being washed and concentrated. The ethereal solution so obtained, which contained no alkaloid, was

* In this connexion it may be noted that the dry, outer layers of the bulb, which are of a fine, silky texture, are used by the natives of South Africa as a substitute for surgical bandages.

extracted successively with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide. The ammonium carbonate extract yielded nothing, but on acidifying the sodium carbonate extracts and again extracting with ether, about 1.5 grams of a product were obtained, which, when distilled under diminished pressure and crystallised from ethyl acetate, proved to be acetovanillone (m. p. 115° . Found, C=65.0; H=6.1. Calc., C=65.1; H=6.0 per cent.).

The occurrence of this substance in Nature appears heretofore only to have been observed in the rhizome of *Apocynum cannabinum*, Linné, and *A. androsaemifolium*, Linné (compare Trans., 1908, **93**, 1513; 1909, **95**, 2863).

The potassium hydroxide extract of the ethereal liquid, from which the acetovanillone had been removed, yielded only a little resinous matter, but, on finally evaporating the ethereal solution, a small amount of a crystalline, neutral substance was obtained. This compound was sparingly soluble in ethyl acetate, from which it separated in colourless needles, melting at $245\text{--}250^{\circ}$.

The aqueous liquid which had been extracted with ether was then shaken repeatedly with amyl alcohol. The liquid so obtained contained a considerable amount of alkaloidal material, which was removed by repeated extraction with dilute hydrochloric acid. The amyl-alcoholic solution yielded only a very small amount of resinous matter.

"Separation of the Alkaloids.

The original aqueous liquid which had been extracted with amyl alcohol was rendered alkaline by the addition of sodium carbonate, and extracted many times with ether, but, as this treatment failed to remove the whole of the alkaloidal material, the alkaline liquid was subsequently extracted with amyl alcohol. The bases contained in the acid, aqueous liquid obtained from the first amyl-alcoholic solution, as above described, were then similarly separated into two portions, one dissolved by ether and the other by amyl alcohol.

The entire amount of bases soluble in ether, dissolved in this solvent, was then extracted with successive portions (20 c.c. each) of 1 per cent. hydrochloric acid. The first eleven extracts were brownish-coloured, slightly alkaline liquids, but the twelfth extraction yielded an acid liquid. The strength of the hydrochloric acid employed for the extraction was then increased to 5 per cent., when, after five more extractions, all the alkaloid had been removed from the ethereal liquid. All the liquids obtained by extraction with 1 per cent. hydrochloric acid yielded, on slow evaporation, only viscous syrups, but the five extracts obtained by

means of the stronger acid all deposited, on keeping, a quantity of solid in the form of wart-like granules. This solid was the hydrochloride of an alkaloid, but it could not be obtained in a definite, crystalline form, nor could any crystalline derivative be prepared from it.

It is thus evident that the alkaloids soluble in ether consisted of at least two bases, one of which was much more strongly basic than the other, and formed by far the greater part of the mixture. This strongly basic product could not be crystallised, nor could any of its salts, but it evidently consisted essentially of a single compound, since, as shown below, it is readily changed by potassium hydroxide, giving a very good yield of a crystalline base. In view of this fact it is considered appropriate to designate it *buphanine*, although no evidence regarding its formula was obtained. Its crystalline hydrolytic product may then be named *buphanitine*.

Formation of Buphanitine, $C_{23}H_{24}O_6N_2$.

A quantity of the amorphous buphanine was heated for two hours on a water-bath with a large excess of alcoholic potassium hydroxide. The greater part of the solvent was then removed, the mixture poured into water, and the base extracted with chloroform. The residue obtained on removing the chloroform was dissolved in alcohol, when it quickly crystallised in colourless prisms, which, on heating at 130° , lost solvent of crystallisation, and then melted at 240° :

0.5573,* on heating at 130° , lost 0.0599 EtOH. EtOH = 10.7.

0.0931 † gave 0.2210 CO_2 and 0.0474 H_2O . C = 64.7; H = 5.6.

0.3915 † „ 22.1 c.c. N_2 (moist) at 22° and 780 mm. N = 6.6.

$C_{23}H_{24}O_6N_2$, EtOH requires EtOH = 10.7 per cent.

$C_{23}H_{24}O_6N_2$ requires C = 65.0; H = 5.6; N = 6.6 per cent.

Buphanitine is very readily soluble in chloroform or ethyl acetate, moderately so in hot alcohol or boiling water, but sparingly soluble in the latter solvents when cold. It cannot be crystallised from water, but separates from this solvent in the form of a jelly.

Buphanitine Hydrochloride, $C_{23}H_{24}O_6N_2 \cdot HCl$.—This salt, prepared by adding hydrochloric acid to an alcoholic solution of the base, crystallised readily from a mixture of ethyl acetate and alcohol in small, colourless needles. It melted and decomposed at 265 — 268° :

0.1815 gave 0.0581 AgCl. Cl = 7.9.

$C_{23}H_{24}O_6N_2 \cdot HCl$ requires Cl = 7.7 per cent.

* Air-dried substance.

† Dried at 130° .

Buphanitine Methiodide, $C_{23}H_{24}O_6N_2, CH_3I$.—This derivative was quickly formed on adding methyl iodide to an alcoholic solution of the base. It crystallised readily from slightly diluted alcohol in slender, glistening prisms, which melted and decomposed at 278° :

0.1582 gave 0.2944 CO_2 and 0.0740 H_2O . $C=50.7$; $H=5.2$.

$C_{23}H_{24}O_6N_2, CH_3I$ requires $C=50.9$; $H=4.8$ per cent.

The alkaline aqueous liquid from which the buphanitine had been removed by means of chloroform was found to contain no acid, but only a very small amount of brown resin. It is thus evident that buphanine is not an ester of buphanitine, and it would appear probable that the latter is formed by the addition of one or more molecules of water to the former.

Isolation of Narcissine, $C_{16}H_{17}O_4N$.

The amyl-alcoholic solution of the bases which were not removed by extraction with ether, as previously described, was evaporated to a low bulk, freed from a small amount of amorphous, non-basic material, and the filtered liquid poured into a large volume of ether. The clear mixture was then washed with water, when a relatively small amount of an alkaloid was removed. This base could not be crystallised, nor could any crystalline salt be obtained from it. The ether-amyl alcoholic liquid was then kept for some time, when a small amount of narcissine separated (m. p. 267°). Found, $C=67.1$; $H=6.0$. Calc., $C=66.9$; $H=5.9$ per cent.).

A direct comparison of this base with a specimen of narcissine obtained from the bulb of the common daffodil, kindly supplied by Mr. A. J. Ewins (compare *Trans.*, 1910, **97**, 2406), confirmed the identity of the two.

Narcissine picrate, $C_{16}H_{17}O_4N, C_6H_3O_7N_3$, has not previously been described. It crystallises readily in bright yellow plates, which decompose and melt at 196 — 199° .

The liquid from which the narcissine had separated was fractionally extracted with hydrochloric acid in a manner similar to that already described, when it was resolved into two products of varying affinity for acid, but the weakly basic material was very small in amount. The first four fractions obtained by shaking with dilute hydrochloric acid were alkaline, and, on keeping, deposited some narcissine, which was removed. The filtrates from this base then yielded small amounts of narcissine hydrochloride, but the greater part of the material contained in them was amorphous, and consisted chiefly of buphanine, since it gave buphanitine on hydrolysis.

Isolation of Chelidonic Acid, C₇H₄O₆.

The alkaline aqueous liquid which had been deprived of alkaloids by means of ether and amyl alcohol, as previously described, was rendered nearly neutral by the addition of hydrochloric acid, and acidified with acetic acid; it was then evaporated under diminished pressure to a small bulk. During this operation about 20 grams of cuprous oxide were deposited. It is evident from this that an unusually large amount of copper was present in the bulb under examination. After removal of the cuprous oxide, the liquid was further evaporated to a syrup, when it was mixed with much hot alcohol, and kept for a few hours. The dark greenish-brown solid which had separated was collected, and washed with dilute alcohol, when it was found to contain an appreciable amount of organic matter, together with copper, sodium, and chlorine. It was dissolved in hot, very dilute alcohol, from which it separated, on cooling, as a brown, partly crystalline powder, free from halogen, although it still contained copper and sodium. This partly purified product was then submitted to a very prolonged extraction in a Soxhlet apparatus with 80 per cent. alcohol, when a colourless solid was slowly removed. The latter was crystallised four times from dilute aqueous hydrochloric acid, when large, colourless, glistening needles of the acid sodium salt of chelidonic acid were obtained (compare Willstätter and Pummerer, *Ber.*, 1904, **37**, 3744). The salt contained water of crystallisation:

0.0942 gave 0.1282 CO₂, 0.0249 H₂O, and 0.0207 Na₂CO₃. C=38.6;
H=2.9; Na=2.2.

C₇H₃O₆Na, C₇H₄O₆, 2H₂O requires C=38.6; H=2.8;
Na=2.4 per cent.

The above-mentioned compound was converted, through the silver salt, into chelidonic acid, which melted and decomposed at 262°. (Found, C=45.5; H=2.3. Calc., C=45.6; H=2.2 per cent.)

The original aqueous-alcoholic filtrate from the crude acid sodium salt of chelidonic acid was fully examined, but nothing crystalline could be separated from it. It readily yielded *d*-phenylglucosazone, and therefore evidently contained sugar. A quantity of it was evaporated as far as possible, and acetylated by means of acetic anhydride, after which the acetyl derivative was dissolved in ether, and freed from a considerable proportion of acidic, resinous matter by means of aqueous alkalis. The purified acetyl derivative, which did not crystallise, was then hydrolysed by means of dilute aqueous sulphuric acid, when a sugar was obtained which could not be crystallised, but, since it was strongly lævorotatory and yielded *d*-phenylglucosazone, it evidently consisted essentially of lævulose.

Examination of the Resin (B).

The resin (B) was a black, wax-like solid, and amounted to 85 grams. It was dissolved in alcohol, and mixed with purified sawdust, after which it was extracted successively in a large Soxhlet apparatus with petroleum (b. p. 35—60°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

The petroleum extract was a black, wax-like mass, and amounted to 56 grams. It was dissolved in ether, and shaken with aqueous ammonium carbonate, when an emulsion was formed, but nothing was dissolved by the alkali. The ethereal solution was separated from the emulsion, and the latter washed repeatedly with ether, after which air was passed through it for some time, when a brown powder separated. This was collected, but it could not be purified by crystallisation, and evidently contained much resinous matter. It appeared, however, also to contain some hydrocarbon, and it was therefore dissolved in hot glacial acetic acid, and deprived of resin by oxidation with a hot solution of potassium permanganate in slightly diluted acetic acid. The mixture was then treated with sulphur dioxide, when it yielded a substance which, after distillation under diminished pressure and crystallisation from ethyl acetate, melted at 75°, and was recognised as pentatriacontane. (Found, C=85.1; H=14.5. Calc., C=85.4; H=14.6 per cent.)

The ethereal liquid from which the emulsion had been separated was then shaken with aqueous potassium carbonate, which removed some fatty acids, and also gave rise to the formation of an emulsion. The fatty acids were converted into their ethyl esters, the latter being distilled under diminished pressure. These esters of the free fatty acids were examined, together with a similar product subsequently obtained from the combined acids.

Isolation of a Phytosterol, C₂₇H₄₆O.

The ethereal liquid which had been deprived of free fatty acids, as above described, was shaken with a solution of potassium hydroxide, but nothing was removed by this treatment. The ether was then evaporated, and the residue heated for two hours with an excess of alcoholic potash, after which the liquid was poured into water, and extracted many times with ether. The ethereal liquid so obtained yielded, on evaporation, a further quantity of pentatriacontane. The mother liquors from this hydrocarbon then gave a product which, on fractional crystallisation from various solvents,

formed long, flattened needles, melting at 132° . This substance, which amounted to about 0.4 gram, gave colour reactions which indicated it to be a phytosterol:

0.1351,* on heating at 110° , lost $0.0068 \text{ H}_2\text{O}$. $\text{H}_2\text{O}=5.0$.

0.1233 † gave 0.3804 CO_2 and $0.1306 \text{ H}_2\text{O}$. $\text{C}=84.1$; $\text{H}=11.7$.

$\text{C}_{27}\text{H}_{46}\text{O}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O}=4.5$ per cent.

$\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C}=84.3$; $\text{H}=11.5$ per cent.

The final mother liquors from which the phytosterol had been obtained yielded only some yellow, uncrystallisable oil of high boiling point.

The alkaline aqueous liquid, from which the phytosterol and hydrocarbon had been removed, was acidified, and extracted with ether, when a quantity of fatty acids was obtained. These were converted into their ethyl esters, and the latter distilled under diminished pressure. The acids obtained from these esters yielded, on crystallisation from ethyl acetate, a mixture of palmitic and stearic acids (m. p. 58°), whilst the mother liquors from this mixture contained some unsaturated acid. A similar result was obtained on examining the acids yielded by the esters of the free fatty acids, previously referred to. The amount of unsaturated acids was not sufficient for their complete examination.

Examination of the Ether, Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The ethereal extract of the resin amounted to 8 grams. On concentrating its ethereal solution, a quantity of a sparingly soluble, brown solid separated. This was collected, and submitted to prolonged extraction in a Soxhlet apparatus with ethyl acetate, when a light-coloured product was obtained. The latter, after crystallisation from dilute pyridine, formed microscopic, colourless leaflets, which melted and decomposed at 286° , and was identified as ipuranol, $\text{C}_{23}\text{H}_{38}\text{O}_2(\text{OH})_2$.

The original ethereal mother liquor, from which the crude ipuranol had been separated, was exhaustively examined, but only amorphous products and a trace of pentatriacontane were obtained from it.

The chloroform, ethyl acetate, and alcoholic extracts of the resin amounted to 9, 1.6, and 5.8 grams respectively, and were found to consist entirely of dark-coloured, resinous products.

Physiological Tests.

The physiological action of the amorphous alkaloids obtained from *Buphane disticha* and that of buphanitine has been investi-

* Air-dried substance.

† Dried at 110° .

gated in the Wellcome Physiological Research Laboratories by Dr. P. P. Laidlaw, to whom the author now expresses his thanks. Narcissine had previously been investigated in this direction (Ewins, *loc. cit.*), and found to be not very toxic.

The strongly basic, amorphous alkaloid, buphanine, produces physiological effects similar to those of hyoscyne and hyoscyamine, particularly the former, but its action is weaker and less lasting than that of either of the last-mentioned bases. It is a mydriatic, and paralyses the salivary secretion and the vagus endings in the heart, and causes death by respiratory failure of central origin. Its action is antagonistic to that of pilocarpine.

Buphanitine is almost inactive, whilst the weakly basic product is a convulsant poison. The amorphous base, which is soluble in water, produced effects reminiscent of those of colchicine and narcissine.

Summary.

The results of the foregoing investigation may be summarised as follows:

The living inner portions of the bulb of *Buphane disticha*, Herb., contain an abundant amount of alkaloid, whilst the dry outer layers are free from such a substance.

An alcoholic extract of the inner portion of the bulbs, when distilled with steam, yielded a small amount of an essential oil containing furfuraldehyde.

The portion of the non-volatile products which was soluble in water yielded a small amount of acetovanillone, a quantity of chelidonic acid, and considerable amounts of copper and lævulose. It also gave a mixture of alkaloids, the principal constituent of which is an amorphous, strongly basic product, designated *buphanine*, which possesses a physiological action similar to that of hyoscyne. A weakly basic and a water-soluble alkaloid were also obtained, together with a small amount of narcissine, $C_{16}H_{17}O_4N$. The weakly basic alkaloid is a convulsant poison, whilst the base soluble in water resembles colchicine and narcissine in its physiological action.

Buphanine, on hydrolysis, is converted into a crystalline alkaloid, *buphanitine*, $C_{23}H_{24}O_6N_2$, which melts at 240° .

The portion of the original extract which was insoluble in water consisted of amorphous products, together with pentatriacontane, a phytosterol, ipuranol, $C_{23}H_{38}O_2(OH)_2$, and a mixture of fatty acids, both free and combined.

CXXXIV.—*Orthophosphoric Acid as a Dehydrating Catalytic Agent. Part I. The Condensation of Acetone in Presence of Phosphoric Acid.*

By PAÑCHĀNAN NEOGI, M.A.

THE condensation of acetone has been largely studied as an example of the conversion of an aliphatic compound into a series of aromatic compounds. The reaction between acetone and concentrated sulphuric acid, according to which mesitylene is formed, has been studied by Kane, Hofmann, Cahours, and others. Baeyer (*Annalen*, 1866, **140**, 297) has shown that when acetone is saturated with hydrogen chloride, and kept for from eight to fourteen days, a heavy, brownish oil separates on the addition of water, consisting mainly of compounds of hydrochloric acid with mesityl oxide and phorone. Pinner (*Ber.*, 1882, **15**, 389; 1883, **16**, 1729) showed later that in addition to mesityl oxide and phorone, xylitone is also formed as a product of condensation of acetone with concentrated hydrochloric acid. Fittig (*Annalen*, 1859, **110**, 32) showed that acetone, when kept in contact with alkali hydroxides, such as potassium hydroxide or quick-lime, condenses to form various condensation products according to the amount of water abstracted, namely, xylite-naphtha, mesityl oxide, mesitylene, phorone, and xylitone. In the present paper the condensation products of acetone with ortho- and meta-phosphoric acids have been studied.

EXPERIMENTAL.

Experiment I.—To 50 c.c. of acetone 40 c.c. of phosphoric acid (D 1.75) were cautiously added. Heat was evolved, and the flask was cooled in water and kept overnight. On distillation next day the greater part of the acetone distilled unchanged, only a small quantity of a yellow oil distilling towards the end of the operation.

Experiment II.—One hundred and fifty c.c. of phosphoric acid were added to 75 c.c. of acetone. Considerable heat was evolved, and the mass turned pale brown. The liquid was kept for two days, and then distilled. During distillation the liquid in the distilling flask separated into two distinct layers. At first, unchanged acetone and water distilled over, followed by a pale yellow oil. After some time, white fumes appeared in the flask, and then the distillation was continued under diminished pressure so long as any liquid passed over. The distillates were mixed, washed with aqueous potassium hydroxide, then with water, and finally dehydrated over

fused calcium chloride. The weight of the yellow oil thus obtained was 23 grams.

The liquid was then fractionally distilled under atmospheric pressure.

No. of fractions.	Weight of liquid. Grams.	Temperature.
1	2.1	110—115°
2	6.2	150—170
3	3.3	190—220
4	6.0	above 250

Experiment III.—A small quantity of the brown, viscous liquid in the distilling flask was decolorised with animal charcoal, and tested for orthophosphoric acid with silver nitrate. The orthophosphoric acid was found to be wholly converted into the pyro- and meta-varieties. To the whole of this liquid 70 c.c. of acetone were added. Heat was evolved as before, and the liquid was again kept for two days, after which time it was distilled under diminished pressure. Two layers were again formed in the distilling flask, which disappeared on cooling. The distillation was continued so long as any liquid passed over. The yellow oil, which floated on water, was then washed and dehydrated as before. The weight of the oil obtained was 20 grams.

On fractional distillation the following fractions were obtained:

No. of fractions.	Weight of liquid. Grams.	Temperature.
1	nil	110—150°
2	4.2	150—170
3	5.5	190—220
4	5.6	above 250

The dark, viscous liquid in the distilling flask was utilised for the third and fourth time by repeating the process with 50 c.c. of acetone each time. The weight of the yellow oil obtained was 22 and 20 grams respectively. When fractionated, the oil yielded fractions similar to those already obtained. Phosphoric acid, being a non-volatile liquid, may be thus utilised repeatedly for abstracting various quantities of water from acetone with the production of various condensation products; in this respect, phosphoric acid has distinct advantages over concentrated sulphuric acid, which decomposes on heating, and chars the acetone employed, and also over the volatile hydrochloric acid used by Baeyer and others. In view of the fact that a given quantity of phosphoric acid is able to convert a large quantity of acetone into its condensation products, attempts were made to ascertain whether its action depended on its dehydrating property or on the formation of intermediate

unstable compounds of phosphoric acid and acetone which would decompose at high temperatures with the elimination of water and the acid itself. The two substances were mixed in the cold, the liquid diluted with water, and neutralised with barium carbonate. Part of the resulting liquid was evaporated, but no solid substance was obtained. The remainder of the liquid was extracted with ether, but no distinct product could be isolated. It seems extremely probable that the non-volatile and dehydrating properties of phosphoric acid (especially pyro- and meta-phosphoric acids) account for its capacity of condensing large quantities of acetone by simply abstracting various quantities of water.

Analyses.

The first fraction, which was not obtained in all cases, was neglected, as it contained unchanged acetone mixed with the liquids of higher boiling points.

Mesityl Oxide, C₈H₁₀O₉.

The second fraction was refractionated, and the liquid, boiling at 131—132°, was analysed. (Found, C=72·56; H=11·13. Calc., C=73·47; H=10·20 per cent.)

Mesitylene.

From the second fraction an almost colourless liquid, boiling at 160—165°, was isolated. It responded to all the well-known tests for mesitylene—boiling point, bromination, nitration, and oxidation. No analysis was, therefore, thought necessary.

Phorone, C₉H₁₄O.

On redistilling the third fraction, a pale yellow liquid, boiling at 197—200°, was obtained. (Found, C=77·61; H=10·82. Calc., C=78·26; H=10·14 per cent.)

Xylitone, C₁₂H₁₈O.

The liquid boiling above 250° was redistilled, and a yellow liquid, boiling at 250—260°, which constituted the bulk of the liquid, was collected and analysed. (Found, C=79·20; H=11·02. Calc., C=80·09; H=10·11 per cent.)

It will thus be seen that the products of condensation in presence of ortho- and meta-phosphoric acids are mesitylene, mesityl oxide, phorone, and xylitone, the liquids of higher boiling points prepon-

derating in quantity, especially in the case of pyro- and metaphosphoric acids. It has already been pointed out that the acid does not char the liquid to a large extent, and that a given quantity of the acid can convert fresh quantities of acetone into its condensation products.

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CXXXV.—*Trialkylammonium Nitrites and Nitrites of the Bases of the Pyridine and Quinoline Series. Part I.*

By PAÑCHĀNAN NEOGI, M.A.

RÂY and Rakshit, in a paper read before the Asiatic Society of Bengal on Dec. 7th, 1910, showed the possibility of the existence of a primary amine nitrite. They have prepared methylammonium nitrite by the interaction of mercuric nitrite and methylamine, and also by the action of silver nitrite on methylamine hydrochloride. In the present paper it is shown that the nitrites of tertiary bases may be prepared by the interaction of silver nitrite and the hydrochlorides of these bases.

Triethylammonium Nitrite.

Solid silver nitrite and triethylammonium chloride were ground together with a little water, and silver chloride was found to be formed immediately. The mixture was transferred to a stoppered bottle. Solutions of the two interacting substances were then added as required, and the bottle vigorously shaken, until a drop of the filtered solution gave no precipitate with either. The filtered solution was left in a desiccator over concentrated sulphuric acid under diminished pressure, when, after a day or two, colourless crystals separated out. When the solution was too dilute, it was concentrated to a small bulk on the water-bath, and then allowed to crystallise in a vacuum desiccator. The yield was almost quantitative.

The crystals are very hygroscopic, extremely soluble in water or absolute alcohol, but very sparingly so in ether. The solution of this salt liberates iodine copiously from a solution of potassium iodide, acidified with dilute hydrochloric or sulphuric acid. That the salt is a pure nitrite was ascertained by the fact that the volume

of nitrogen yielded by the "urea" method was identical with the volume of nitric oxide obtained by the Crum-Frankland process. On heating with dilute potassium or sodium hydroxides, the tertiary amine is formed, which can easily be recognised by its characteristic odour.

The actual composition of the salt was determined by the "urea" method, which gives very accurate results. The salt decomposed with such explosive violence in the combustion tube that little value could be assigned to the results of combustion analysis. It was powdered and dried in a vacuum desiccator over sulphuric acid so long as it remained colourless. It was then analysed by the "urea" method, and the results corresponded with the formula $N(C_2H_5)_3HNO_2 \cdot H_2O$.

0.1246 gave 18.1 c.c. N_2 (moist) at 23° and 755 mm., whence "nitritic" nitrogen = 8.1. Calc. = 8.4 per cent.

Some of the salt was next kept for two days in the vacuum desiccator over sulphuric acid until it became white. When analysed by the "urea" method, it was found to correspond with the formula of the anhydrous compound, $N(C_2H_5)_3HNO_2$.

0.2062 gave 37.8 c.c. N_2 (moist) at 23° and 755 mm., whence "nitritic" nitrogen = 10.2. Calc., 9.4 per cent.

When kept for a longer period the salt decomposes, forming the nitrate.

Sublimation of Triethylammonium Nitrite.

The hydrated crystals contained in a long, hard glass tube were heated in a sulphuric acid bath, the tube being connected with a vacuum pump. Under a pressure of 10—20 mm. the salt was found to melt at about 60° , and minute drops of water collected in the cooler parts of the tube. At about 70 — 75° beautiful, foliated, needle-like crystals began to appear in the cooler parts, and a good portion of the salt thus gradually sublimed with partial decomposition, a small quantity of a brown liquid remaining at the bottom of the tube. The sublimed salt, on analysis, was found to be triethylammonium nitrite.

The salt was next submitted to steam distillation, and it was found that it distilled with steam in appreciable quantities, especially under diminished pressure.

The question whether the sublimation of the nitrite is a case of dissociation or not is being studied by determining its vapour density by Hofmann's method. On gently heating the salt in an open tube over the naked flame, it decomposes with almost explosive violence, evolving nitrous fumes.

Pyridinium Nitrite.

The nitrite of the tertiary base, pyridine, has been prepared in a state of solution. Ice-cold solutions of pyridine hydrochloride and silver nitrite were treated in the same manner as above. The resultant liquid was faintly acid, and did not liberate iodine on the addition of potassium iodide; but on the addition of a dilute acid, iodine was copiously set free. The liquid could not be concentrated over the water-bath, and when crystallised over sulphuric acid in a vacuum desiccator yielded needle-shaped crystals of the nitrate.

The solution of the nitrite is unstable, and on keeping for some days gradually decomposes, forming the nitrate, as can be easily ascertained by the increase of nitric oxide by the Crum-Frankland method, and decrease of "nitritic" nitrogen by the "urea" method, the volumes of the two gases being originally equal.

Other salts of the series are either under preparation or examination.

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CXXXVI.—*The Absorption Spectra of Cinchonine, Quinine, and their Isomerides.*

By JAMES JOHNSTON DOBBIE and ALEXANDER LAUDER.

THE investigation described in this paper was undertaken originally with the object of ascertaining whether the absorption spectra of cinchonine and its isomerides α -, β -, and allocinchonine differ from one another in such a way as to imply differences in the structure of these alkaloids, or are identical, as one would expect them to be if the alkaloids possessed the same structure. We found the spectra to be indistinguishable, but, for reasons to be explained hereafter, it is impossible to infer from their identity that the alkaloids in question are stereoisomerides. The investigation, however, has yielded results of considerable interest in other directions.

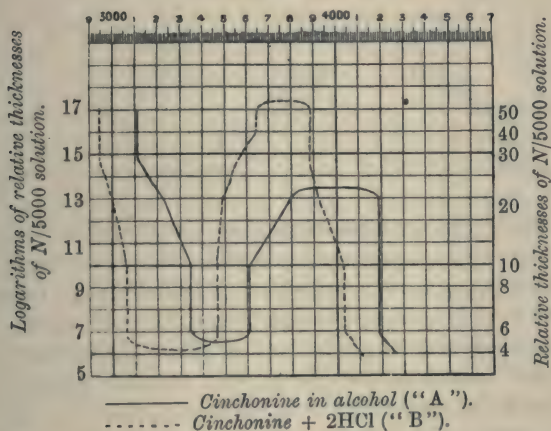
The absorption spectra of cinchonine and quinine were first examined by Hartley (*Phil. Trans.*, 1885, 175, 471), and afterwards by ourselves (*Trans.*, 1903, 83, 605).

In the course of the present investigation we had occasion to

examine the spectra of solutions of these alkaloids and of some of their compounds and derivatives in a variety of solvents. It then became evident that each alkaloid, with its related compounds and derivatives, exhibits two distinct series of spectra, one agreeing with, and the other differing considerably from, the spectra described in connexion with our earlier work on the subject.

In the case of cinchonine the spectra of an alcoholic solution or of salts containing one equivalent of acid to one of the base, for example, $C_{19}H_{22}ON_2 \cdot HCl$, may be taken as representing the one series, and the spectra of salts containing two equivalents of acid to one of base, for example, $C_{19}H_{22}ON_2 \cdot 2HCl$, the other (Fig. 1).

FIG. 1.

Oscillation frequencies.

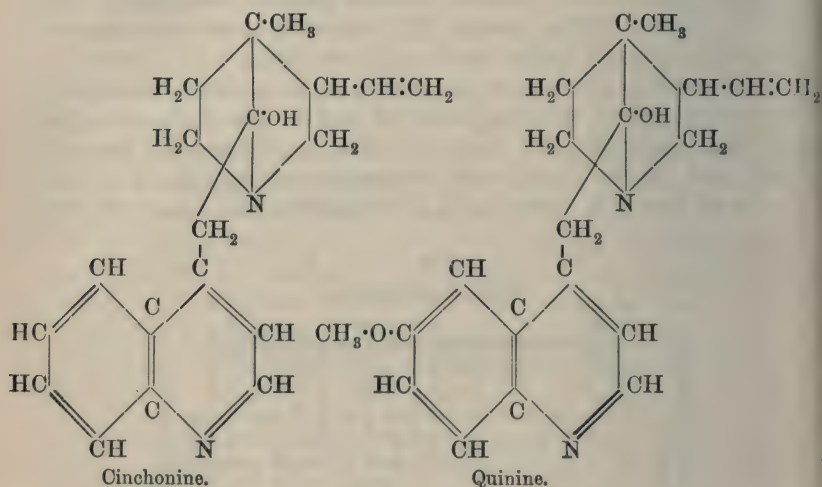
For convenience we shall refer hereafter to the former as spectrum "A," and to the latter as spectrum "B."

In spectrum "A" the absorption band is neither well defined nor persistent; with a layer 20 mm. thick of $N/5000$ -solution the band lies between $1/\lambda$ 3220 and $1/\lambda$ 3824. In spectrum "B," on the other hand, the general absorption is greater, and the absorption band is well defined and much more persistent; with a layer of 20 mm. thick of a $N/5000$ -solution the band lies between $1/\lambda$ 3000 and $1/\lambda$ 3488.

The clue to the explanation of the difference between the two series of spectra was afforded by the study of the alkyl derivatives. According to von Miller and Rohde's formula for cinchonine,* this

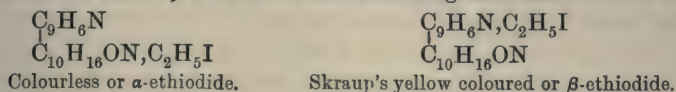
* The recent work of Rabe on cinchonine shows that the formulæ here given for cinchonine and quinine probably require modification; the alterations, however, which he suggests do not affect the points dealt with in this paper.

alkaloid contains two atoms of nitrogen, one belonging to the quinoline nucleus, the other to that part of the molecule commonly referred to as the "second half":



Both atoms of nitrogen are capable of combining with an equivalent of acid or with a molecule of alkyl haloid. The "second half" of the cinchonine molecule is, however, more basic than the quinoline nucleus, and if only one equivalent of acid be added to a molecule of the alkaloid it is to the nitrogen of the "second half" that it attaches itself. Skraup and Konek von Norwall (*Monatsh.*, 1894, **15**, 37) established this point in the following manner. By heating cinchonine hydriodide, $C_{19}H_{22}ON_2 \cdot HI$, with ethyl iodide, and treating the compound formed with ammonia, they obtained a yellow-coloured ethiodide, which differs entirely from the earlier known colourless ethiodide obtained by heating a solution of cinchonine in alcohol with ethyl iodide. The yellow ethiodide possesses the properties of a true quinoline compound. That the alkyl haloid group which it contains is attached to the nitrogen of the quinoline nucleus is placed beyond doubt by the fact that when heated with silver nitrate to remove the iodine and then oxidised with permanganate in the cold, it yields cinchoninic acid ethyl nitrate, $CO_2H \cdot C_9H_6N \cdot C_2H_5 \cdot NO_3$. It follows that the colourless ethiodide obtained by the direct action of ethyl iodide on cinchonine has the alkyl haloid united to the nitrogen of the "second half," and that it is to this nitrogen atom that acids attach themselves when present only in the proportion of one equivalent.

lent to one molecular weight of the alkaloid. The relation of the two ethiodides is easily seen from the following formulæ:



We have repeated Skraup's experiments, and have photographed the spectrum of his ethiodide, and compared it with that of the α -ethiodide with the following results.

Cinchonine α -ethiodide gives the spectrum "A" in alcoholic solution, but the spectrum "B" in acid solution. On the other hand, Skraup's β -ethiodide gives spectrum "B" in alcoholic solution, and the spectrum remains unchanged on the addition of acid. The diethiodide of cinchonine, $\text{C}_{19}\text{H}_{22}\text{ON}_2, 2\text{C}_2\text{H}_5\text{I}$, gives the spectrum "B."

Having regard to the results obtained from the examination of the salts and of the alkyl haloid derivatives of cinchonine, it is clear that so long as the nitrogen of the quinoline nucleus is not in combination with acid or alkyl haloid, the spectrum "A" is obtained, but that when it is so combined the spectrum "B" is obtained, whether the nitrogen of the "second half" is in combination with acid or alkyl haloid or not. In other words, whether the spectrum "A" or "B" is produced depends entirely on the condition of the nitrogen of the quinoline nucleus as regards valency. Spectrum "A" is associated with the tervalent, spectrum "B" with the quinquevalent condition.

In his paper on the absorption spectra of the alkaloids (*loc. cit.*), Hartley pointed out that the position of the absorption band in the spectra of the cinchona alkaloids agrees with that of quinoline. As, however, the curves in his paper and those illustrating the paper in which the spectrum of quinoline is described (*Trans.*, 1885, **47**, 685) were not drawn on the same system, no exact comparison of them was possible.

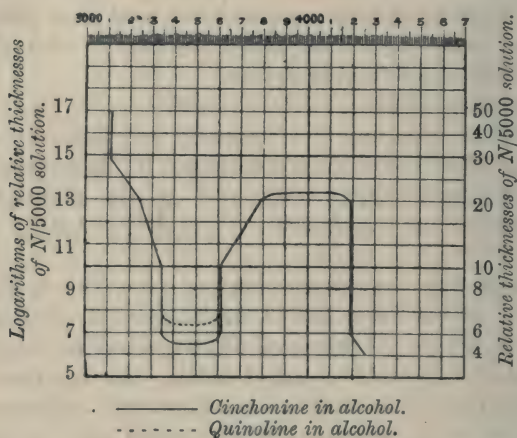
It was not until we had engaged in the present investigation and re-photographed the spectra, both of quinoline and of cinchonine (Figs. 2 and 3), that the close agreement of the absorption curves of the two substances became evident to us.

On comparing them it will be seen that they coincide almost exactly, and that the only difference is that the absorption is a little greater in the case of cinchonine than in that of quinoline. The spectrum "A" of cinchonine, as well as of certain of its derivatives and salts, is practically the same as the spectrum of quinoline, whilst the spectrum "B" of other cinchonine salts and derivatives is practically the same as that of the quinoline salts. The character,

therefore, of the cinchonine spectrum depends almost entirely on the quinoline part of the molecule, and is hardly at all affected by the "second half."

FIG. 2.

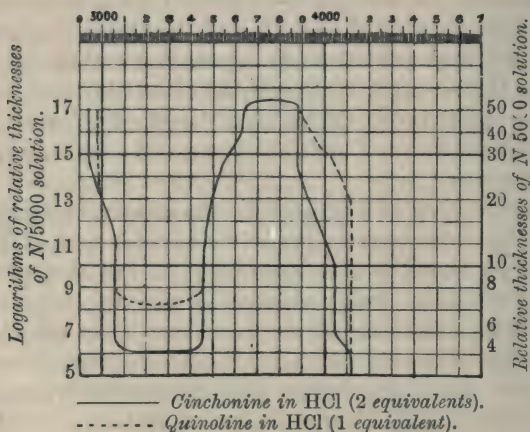
Oscillation frequencies.



This result, at first sight surprising, is in no way at variance with our previous knowledge of the relations existing between

FIG. 3.

Oscillation frequencies.



absorption spectra and chemical constitution. Although some of the details of the structure of cinchonine are still the subject of controversy, it has been established that the ring or rings of the

"second half" of the molecule are completely reduced. It is also a well ascertained fact that reduced rings produce no absorption band, but act like open chains so far as absorption is concerned. The only effect, therefore, which, *a priori*, we should expect the "second half" of the molecule to produce on the absorption spectrum of the quinoline nucleus would be to increase somewhat the amount of general absorption, and this is what we actually find to be the case. The only matter for surprise is that the effect in this direction is so slight.

We are now in a position to explain why it is that a change within the "second half," such as the alteration of the valency of the nitrogen atom, produces no effect on the spectrum, while the corresponding change in the case of the nitrogen atom of the quinoline nucleus produces so marked an effect. The fact that the vinyl group in cinchonine belongs to the "second half" of the molecule affords a more complete explanation of the practical identity of the spectrum of cinchotenine with that of cinchonine than the one formerly advanced by us (*loc. cit.*).

It is interesting to note that whilst the quinoline alkaloids derived from the cinchona bark show only one or two types of spectra, the *isoquinoline* alkaloids, nearly all of which have unreduced rings attached to the *isoquinoline* nucleus, possess highly characteristic spectra, differing widely from one another, as well as from those of *isoquinoline*.

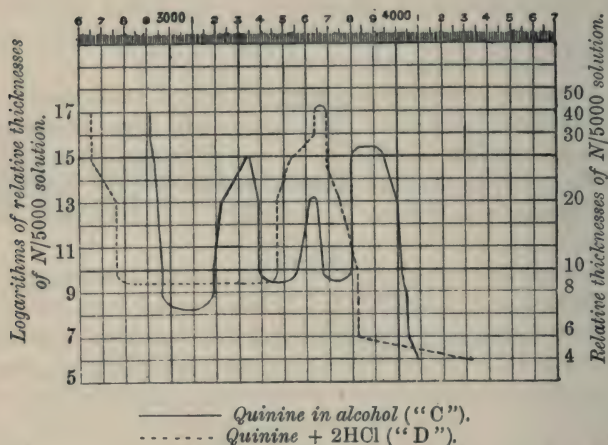
The conclusions arrived at from the chemical investigation of the constitution of cinchonine and those derived from the spectrographic examination, are thus seen to be in complete agreement.

Before we had discovered the close connexion which we now know to exist between the spectra of cinchonine and quinoline, or had succeeded in accounting for the difference between the spectra "A" and "B," we had undertaken, with the object explained at the beginning of this paper, a spectroscopic investigation of the artificial isomerides of cinchonine, the claim of which to be regarded as true chemical individuals has been well established, as well as of the naturally-occurring isomerides, cinchonidine and homocinchonidine. All these substances give spectra "A" and "B" practically identical with those of cinchonine; but it is obviously impossible to infer from this that they are stereoisomerides, and not structural isomerides, in view of the fact that the "second half" of the cinchonine molecule as a whole produces such a small effect on the quinoline spectrum, and that such an important change as the conversion of tervalent nitrogen into quinquivalent nitrogen or of a vinyl into a carboxyl group may take place in this part of the molecule without producing any appreciable effect on the spectrum.

Quinine is distinguished from cinchonine by the possession of a methoxy-group in the quinoline nucleus, and, as may be seen from a comparison of the curves in Figs. 1 and 4, there is a considerable difference between the spectra of the two compounds. Like cinchonine, quinine exhibits two series of spectra, "C" and "D," which are related to one another in the same way as the cinchonine spectra.

The spectrum "C" is given by an alcoholic solution of quinine, and by solutions of quinine salts containing one equivalent of acid to one molecular proportion of alkaloid; spectrum "D" by solutions of salts containing two equivalents of acid to one molecular proportion of the alkaloid. In spectrum "C" with layers 20 mm.

FIG. 4.
Oscillation frequencies.



thick of $N/5000$ -solution the principal band lies between $1/\lambda$ 2938 and $1/\lambda$ 3293. In spectrum "D" the general absorption is greater and the band is wider; with layers 20 mm. thick of a $N/5000$ -solution the band lies between $1/\lambda$ 2768 and $1/\lambda$ 3468.

The substances examined were either prepared in the laboratory or purchased from well known makers. In nearly every case two preparations of independent origin were examined. The following table contains a list of the substances the spectra of which were photographed in connexion with the present investigation, and shows the spectrum obtained in each case—(a) when the substance was photographed in alcoholic solution or in a solution containing not more than one equivalent of acid to one molecular proportion of base, and (b) in a solution containing at least two equivalents of

acid to one of the base. The letters A, B, C, and D refer to the figures in the text bearing these letters.

	Spectrum.	
	(a).	(b).
<i>Cinchonine</i> . Recrystallised from alcohol, m. p. 254°.		
Other specimens were also examined with identical results.....	A.	B.
<i>Cinchonidine</i> , m. p. 202°.....	A.	B.
<i>Homocinchonidine</i> , m. p. 201°.....	A.	B.
<i>α</i> - <i>Cinchonine</i> . Prepared by Hesse's method (<i>Annalen</i> , 1893, 276, 91), m. p. 126—127°	A.	B.
<i>β</i> - <i>Cinchonine</i> . Prepared by Skraup's method (<i>Monatsh.</i> , 1900, 21, 393), m. p. 125°	A.	B.
<i>lloCinchonine</i> Prepared by Hlavnicka's method (<i>Monatsh.</i> , 1901, 22, 191), m. p. 218—220°	A.	B.
<i>Cinchotenine</i> , m. p. 195°	A.	B.
<i>Cinchonamine</i> , m. p. 186°	A.	B.
<i>α</i> - <i>Cinchonine methobromide</i> . Prepared by Claus and Müller's method (<i>Ber.</i> , 1880, 13, 2290), m. p. } 261—262°	A. (alcoholic solution).	B. (+1 equiv. acid).
<i>Hydriodide of β-cinchonine ethioidide</i> , m. p. 251°	B.	B.
<i>β</i> - <i>Cinchonine ethioidide</i> (C ₂ H ₅ I attached to quinoline N). Prepared by Skraup's method (<i>Monatsh.</i> , 1894, 15, 37), m. p. 184°	B.	B.
<i>Cinchonine diethioidide</i> . Prepared by Skraup and Konek von Norwall's method (<i>Monatsh.</i> , 1894, 15, 43), m. p. 264°	B.	B.
<i>Cinchonine chloride</i> , C ₁₉ H ₂₁ N ₂ Cl. Prepared by Com- stock and König's method (<i>Ber.</i> , 1884, 17, 1984), m. p. 72—73°	A.	B.
<i>Quinoline</i> . (1) Synthetical; (2) Prepared from } cinchonine	A. (alcoholic solution).	B. (+1 equiv. acid).
<i>Quinoline methioidide</i>	B.	B.
<i>Quinine</i> , m. p. 175·5°	C.	D.
<i>Quinine methioidide</i> , m. p. 98°.....	C. (alcoholic solution).	D. (+1 equiv. acid).
<i>Quinine dimethioidide</i> . Prepared by Claus and Mall- mann's method (<i>Ber.</i> , 1881, 14, 76), m. p. 167—168°	D.	D.

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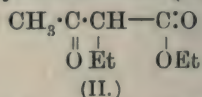
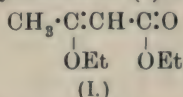
CXXXVII—*The Influence of Conjugated Linkings on General Absorptive Power. Part II. Some Open-chain and Cyclic Compounds.*

By CECIL REGINALD CRYMBLE, ALFRED WALTER STEWART,
ROBERT WRIGHT, and FLORENCE WILLIAMSON REA.

IN the previous paper of this series (this vol., p. 451), it was shown that on examining the absorption spectra of two isomeric substances, the one containing in the side-chain double bonds which are conjugated with the nucleus will have a greater absorptive power than the isomeride in which the nucleus is isolated from the double bond in the side-chain by such a group as the methylene radicle. The results given in the present communication show that a similar effect is observable in the open-chain and cyclic series.

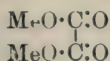
(a) *Open-chain Compounds.*

Baly and Desch (Trans., 1904, **85**, 1035) examined the spectra of the two isomeric ethyl derivatives of ethyl acetoacetate, namely, ethyl ethoxycrotonate (I) and ethyl ethylacetoacetate (II):

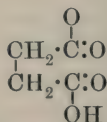


It will be observed that in the formula (I) the double bond of the carbonyl in the carboxyl group is conjugated with the ethylenic double bond; whereas in the formula (II) no such conjugation of the double bonds is present, the two carbonyl groups being separated by the group $\cdot\text{CHEt}\cdot$. Baly and Desch state that whilst the enolic form (I) gives marked absorption, the ketone (II) is practically diactinic at the same dilution. Thus the presence of the conjugated double bonds in this case coincides with a great increase in general absorptive power.

In the case of dibasic acids, we have examined two pairs of isomerides. If the formula of methyl oxalate is compared with that of succinic acid it is obvious that in the case of the oxalate the two carbonyl groups are conjugated, whilst in succinic acid they are separated from one another by the interposition of the two methylene radicles:



Methyl oxalate.

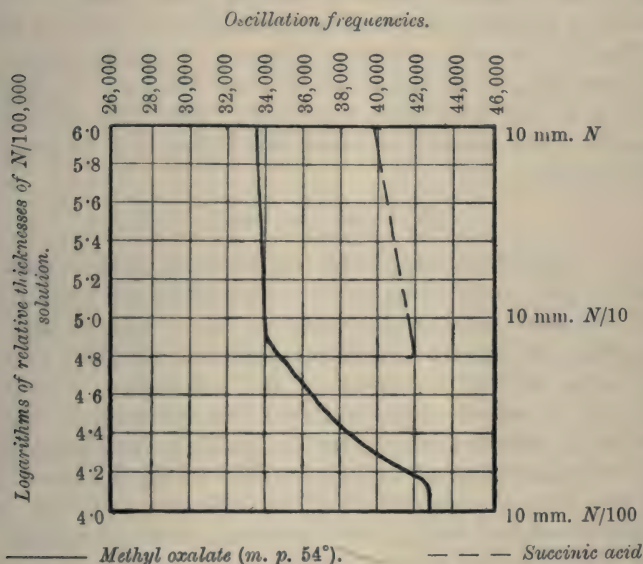


Succinic acid.

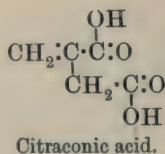
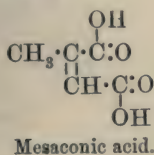
An inspection of the curves in Fig. 1 will show that the general absorptive power of the oxalate much exceeds that of the isomeric succinic acid.

A third example may be quoted, in which there are three double linkings in the molecule. It has been shown by one of us (Stewart, Trans., 1907, **91**, 207) that the absorptive power of mesaconic acid greatly exceeds that of itaconic acid. In the formula of the former there are three conjugated double bonds; whereas in the latter the

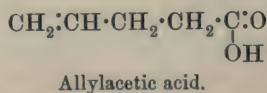
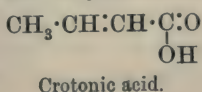
FIG. 1.



bond in one of the carbonyl radicles is separated from the rest of the molecule by a methylene group, and hence does not enter into the conjugation:



The influence of conjugation can also be traced in the cases of crotonic and allylacetic acids:



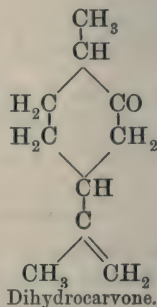
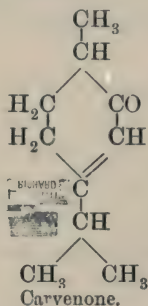
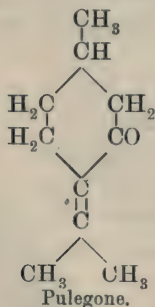
As a rule, general absorption increases with increased molecular weight; thus the higher members of a homologous series are more absorptive than the lower. Since allylacetic acid contains one methylene group more than crotonic acid, one might expect it to show more general absorption than the latter substance. We have found, however, that allylacetic acid is practically diactinic, whilst crotonic acid has very strong general absorption (Stewart, *Trans.*, 1907, **91**, 203). This apparent anomaly is easily explicable; for crotonic acid contains two conjugated double bonds (the carbonyl and the ethylenic), whereas in allylacetic acid the double bonds are separated from each other by two methylene radicles. Thus the influence of conjugation in this case is sufficiently strong to outweigh the effect of the extra methylene group in allylacetic acid.

It seems clear from the above evidence that we are justified in assuming in the open-chain compounds that connexion between conjugation and absorption which was found to hold good in the aromatic series.

(b) *Cyclic Substances.*

In the closed-chain compounds we revert to some extent to the aromatic type; and in this case we must make the same postulate which was laid down in the previous paper with regard to the examination of the general absorptive power. In order to compare the general absorptive powers of two substances, care must be taken not to include those parts of the spectrum in which the influence of selective absorption is manifest; but those portions must be examined which are not exposed to the confusion arising from the mutual interaction of the vibration causing general absorption and that which gives rise to selective absorption.

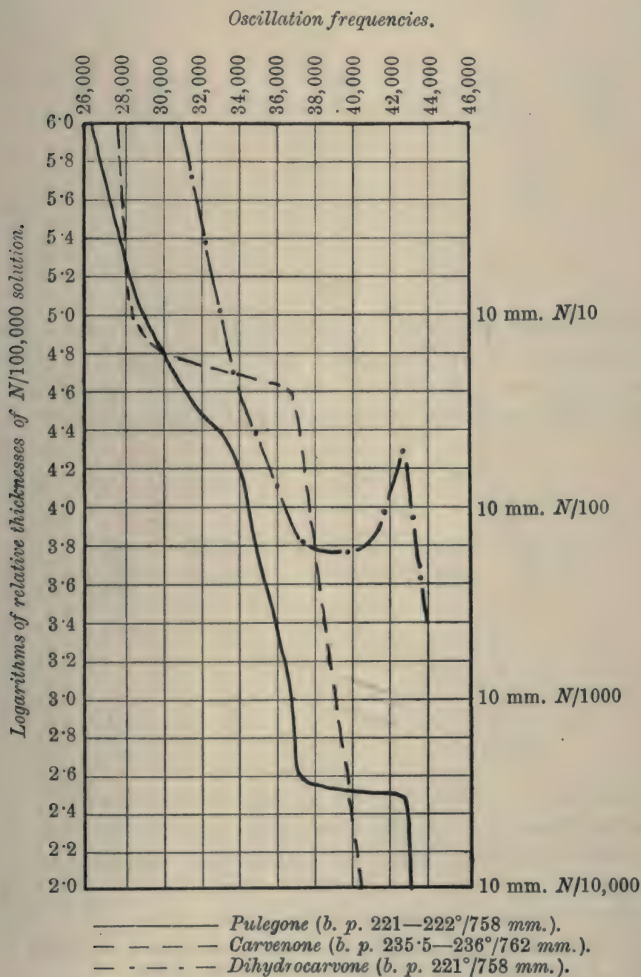
The first isomerides with which we may deal are pulegone, carvenone, and dihydrocarvone:



A glance at the formulæ will show that in both pulegone and carvenone an ethylenic linking is conjugated with the double bond

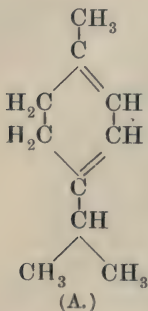
of a carbonyl group; whilst in dihydrocarvone the double bonds are separated by a methylene radicle. Inspection of the curves in Fig. 2 will show that the two former substances have much greater general absorptive power than dihydrocarvone. (The rapid exten-

FIG. 2.

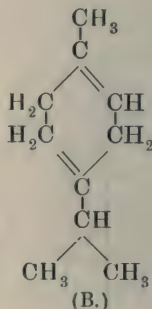


sions of the curves between the abscissæ 36 and 40 are obviously due to selective absorption, so that a true comparison of the general absorptive power of the substances is only to be made by examining the curves above this region.)

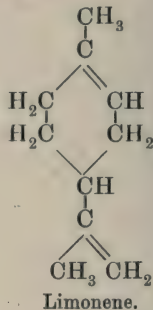
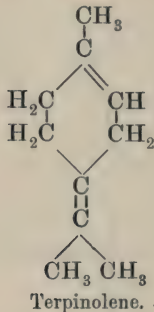
In this connexion, it was thought to be of interest to photograph the absorption spectra of terpinolene, terpinene, and limonene in order to see if some light could be thrown on the constitution of terpinene. Harries (*Ber.*, 1902, **35**, 1169) has shown that terpinene must have either of the formulæ (A) or (B):



Terpinene.



From chemical evidence he regards (B) as the most probable. An examination of the absorption spectra of the three substances confirms this view. In Fig. 3 are given the curves of the three isomeric forms, terpinene, terpinolene, and limonene:



In limonene, the double bonds are separated from each other by two carbon atoms; in terpinolene, only one carbon atom divides them. The absorptive power of terpinolene is greater than that of limonene. Now the absorptive powers of terpinolene and terpinene are almost identical, as the curves show, but if terpinene had the formula (A) above, it would contain a system of two conjugated double bonds; and hence we should expect its absorptive power to exceed that of terpinolene. If terpinene has the formula (B), its double bonds will be in the 1:4-position with regard to each other, which is the same as the relation of the bonds in terpinolene. Of course, in terpinolene one double bond is outside the ring, whilst they are both in the terpinene ring. From

the close similarity between the spectra of terpinolene and terpinene it seems reasonable to assume that the formula for terpinene is:

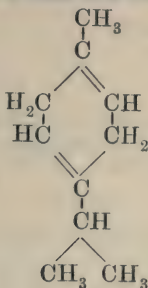
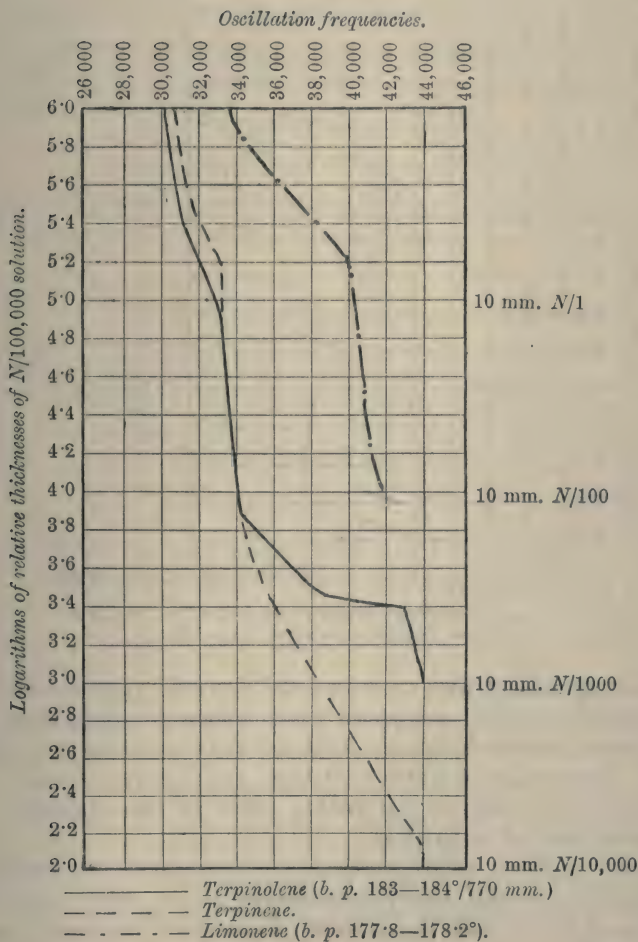
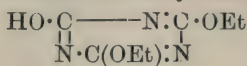


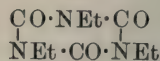
FIG. 3.



In the heterocyclic series we have examined the two substances, ethyl cyanurate and ethyl isocyanurate:



Ethyl cyanurate.

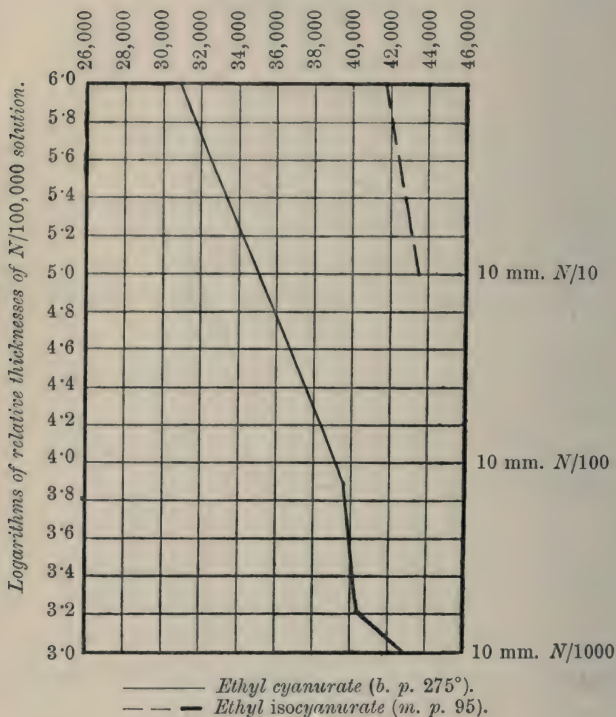


Ethyl isocyanurate.

and as the curves in Fig. 4 show, the normal compound has a much greater power of general absorption than its isomeride. This

FIG. 4.

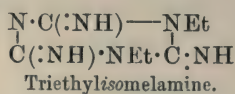
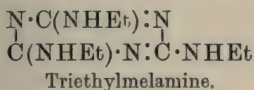
Oscillation frequencies.



is quite in agreement with our views, for it is clear from the formulæ above that the normal compound has a system of conjugation akin to that of the benzene nucleus, whilst the *iso*-form has no conjugation at all. The results of Hartley, Dobbie, and Lauder (Trans., 1901, 79, 854) in the case of the methyl esters of the cyanuric acids give curves similar to our own.

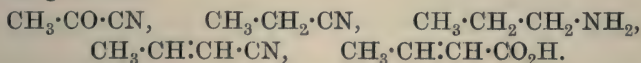
Hartley, Dobbie, and Lauder (*ibid.*) examined the spectra of triethylmelamine and triethylisomelamine; and here again the influence of conjugation is apparent. The normal compound (which

contains the conjugated system) has a greater general absorption than the *iso*-form (which is unconjugated):



From the results contained in the present paper and its predecessor, it seems very probable that the rule which we laid down is a general one. We have examined the absorption curves of thirty-nine substances, and in every case it has been found that a compound containing conjugated double bonds has a greater power of general absorption than the corresponding unsaturated substance.

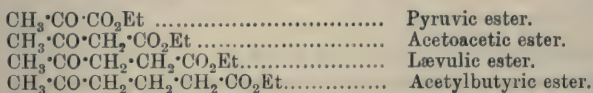
In this department of the subject we propose to attempt a classification of double bonds with respect to their power of influencing general absorptive power. For example, a comparison of the spectra of such series as those shown below might lead to interesting results:



Some experiments in this direction have already been begun, and we hope to publish a further communication on this point.

(c) *Special Contiguity of Unsaturated Groups.*

In connexion with the foregoing results, it seemed to us of interest to examine the effect of two unsaturated radicles on each other when, according to the van't Hoff-Wislicenus view, they are so placed in a carbon chain as to be near to each other in space. For the sake of convenience, we may term this phenomenon space-conjugation. Hilditch (*Trans.*, 1909, **95**, 1581) has shown that when optically active salts of the dibasic acids of the fatty series are examined, an anomaly is found in those substances in which the optically active portions of the molecule approach each other in space. We have examined one series of this type in which space-conjugation might be expected, namely, the ketonic acids:



In the case of pyruvic ester we have simple conjugation of the two carbonyl radicles, and their interaction is so strong as to produce an absorption band in the spectrum. This band is not found in either acetoacetic ester or lævulic ester. In acetylbutyric ester we had expected to find traces of the influence of space-conjugation of the two carbonyl groups; but none was detected,

either in general absorption or in the presence of an absorption band. We propose, however, to continue this branch of the investigation with other series.

Conclusions.

(1) It has now been established that if the absorption of two isomeric substances containing more than one double bond be examined, the isomeride which contains the greater degree of conjugation will have the greater power of general absorption.

(2) Up to the present it has not been possible to trace the effect of space-conjugation in the case of carbonyl groups.

We desire to express our thanks to the Research Fund Committee of the Society for a contribution towards the expenses of this research.

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THE QUEEN'S UNIVERSITY OF BELFAST.

CXXXVIII.—*New Derivatives of Aminolauronic Acid.*

By JOHN WEIR, M.A., B.Sc., Ph.D. (Carnegie Fellow).

THE following research was undertaken with the view of preparing, by substituting aminolauronic acid for anthranilic acid in the well-known indigotin synthesis, the camphor analogue of indigotin,

$\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C}_8\text{H}_{14}$. The special object of the work was

the preparation of a series of optically active compounds corresponding with those obtained as intermediate products in the conversion of anthranilic acid into indigotin. For example, the analogues of indoxyl and indigo-white would be :

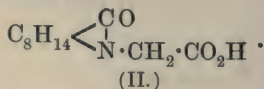
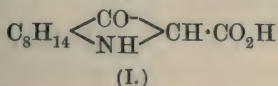


respectively, and it was hoped that the polarimetric study of these substances under different conditions would throw some light on the tautomeric changes undergone by compounds of this type.

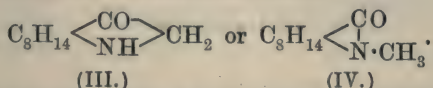
Unfortunately it was found impossible to effect the desired synthesis on the lines indicated, but in the course of the work several new derivatives of aminolauronic acid have been prepared, which are not without interest and are here described.

Aminolauronic acid (Noyes, *Amer. Chem. J.*, 1896, 16, 506) was found to undergo condensation with monochloroacetic acid, giving *carboxymethylaminolauronic acid*, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (m. p.

183—184°), which on fusion lost one molecular proportion of water, and gave a monobasic acid melting at 142—143°. The two possible formulæ for the latter substance are therefore :

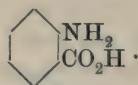
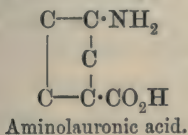


Of these alternatives, only a compound corresponding with formula (I) is suitable for the suggested synthesis. The elimination of the carboxyl group was effected by dry distillation of the barium salt of the acid intimately mixed with barium hydroxide. The orange-coloured oily product thus obtained slowly solidified to a dark red wax, which gave analytical figures agreeing with those calculated for $\text{C}_{10}\text{H}_{17}\text{ON}$, and therefore has the constitution



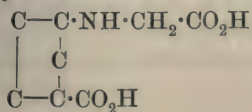
As no derivative corresponding with a nitrosoamine could be obtained from the substance by the action of nitrous acid, its structure is probably that indicated by formula (IV); moreover, on heating the compound with concentrated hydrochloric acid in a sealed tube, no trace of ammonium chloride was formed. It follows that the product obtained on fusing carboxymethylaminolauronic acid must have the constitution represented by formula (II) above, and is therefore *N-anhydrocarboxymethylaminolauronic acid*. The product of the subsequent distillation with barium hydroxide will thus be *N-anhydro-methylaminolauronic acid*.

This result, although it excludes the possible synthesis of "camphor-indigo" on the lines suggested, is not altogether in disagreement with that obtained in the indigotin synthesis from anthranilic acid, as it must be remembered that aminolauronic acid may be regarded as a meta-substitution derivative of a pentamethylene ring, whereas, on the other hand, anthranilic acid is an ortho-derivative of benzene. The essential differences in type are shown below :

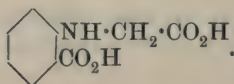


Anthranilic acid.

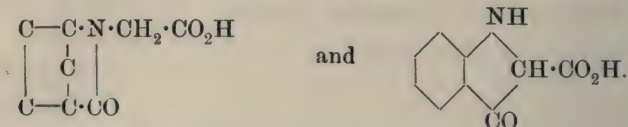
Adopting the above skeleton formulæ, the products obtained from each by condensation with monochloroacetic acid are respectively :



and



The loss of a molecular proportion of water yields in both instances compounds containing a pyrrole ring, namely,



acid, $C_8H_{14} \begin{smallmatrix} CO \\ \diagup \\ N \\ \diagdown \end{smallmatrix} Bz$. This ring-formation was again accompanied by a pronounced change in optical activity.

	Solvent	$[\alpha]_D^{18}$.
Benzoylaminolauronic acid	Alcohol	- 18.4°
Methylbenzoylaminolauronate	Alcohol	- 28.9
N-Anhydrobenzoylaminolauronic acid.....	Alcohol	- 69.1

EXPERIMENTAL.

Aminolauronic Acid Hydrochloride.

This compound has already been described by Noyes (*loc. cit.*), but as the following method of preparation seems in many ways an improvement on the original process, it is described in detail.

Finely powdered camphoric anhydride (100 grams) was dissolved with constant shaking in one litre of concentrated ammonia solution. The clear liquid so obtained was freed from excess of ammonia by heating at 20°/15 mm., and then rendered acid by the addition of hydrochloric acid. The precipitated camphoramic acid weighed 100 grams (Auwers and Schnell, *Ber.*, 1893, **26**, 1522).

This crude product was converted into aminolauronic acid according to Noyes' directions, sodium hypochlorite being, however, used in place of sodium hypobromite.

Cold solutions of camphoramic acid (1 mol.) and sodium hypochlorite (1 mol.) in sodium hydroxide (3 mols.) were gradually mixed, and the mixture heated for a short time on a water-bath. After cooling, the liquid was acidified with concentrated hydrochloric acid (4 mols.), the solvent removed at 30°/15 mm., and the residue extracted several times with boiling alcohol—preferably in a Soxhlet's apparatus. The alcoholic extract was evaporated to dryness at 25°/15 mm., and the crystalline residue purified by dissolving it in hot water and adding excess of acetone. By this means 70 grams of pure aminolauronic acid hydrochloride (m. p. 303°) were obtained from 100 grams of camphoramic acid.

The specific rotation of the compound was determined both in aqueous and in alcoholic solution :

Solvent.—*Water* : $c = 1.437$, $l = 2$, $\alpha + 0.75^\circ$, $[\alpha]_D^{18} + 26.1^\circ$.

„ *Alcohol* : $c = 1.335$, $l = 2$, $\alpha + 0.71^\circ$, $[\alpha]_D^{18} + 26.6^\circ$.

Carboxymethylaminolauronic acid, $CO_2H \cdot C_8H_{14} \cdot NH \cdot CH_2 \cdot CO_2H$.

Fifty-five grams of aminolauronic acid hydrochloride (1 mol.) and 26 grams of monochloroacetic acid (1 mol.) were dissolved in 320 c.c. of a 10 per cent. solution of sodium hydroxide (3 mols.), and the mixture

gently boiled on a glycerol bath for five hours. After cooling and acidifying with hydrochloric acid, the product was precipitated as a crystalline powder, which was purified by recrystallisation from methyl alcohol containing a little water. Yield 50 grams. The compound is readily soluble in water, but sparingly so in organic media.

It crystallises with two molecules of water of crystallisation:

0.3483 lost 0.0442 at 110° . $H_2O = 12.7$.

$C_{11}H_{19}O_4N \cdot 2H_2O$ requires $H_2O = 13.3$ per cent.

Analysis of a specimen dried at 110° gave:

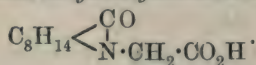
Found, $C = 57.5$; $H = 8.43$; $N = 6.07$.

$C_{11}H_{19}O_4N$ requires $C = 57.6$; $H = 8.30$; $N = 6.01$ per cent.

Solvent.—*Water*: $c = 1.445$, $l = 2$, $\alpha + 1.32^{\circ}$, $[\alpha]_D^{18} + 45.7^{\circ}$.

On heating the compound, it fuses with effervescence at about 183° , the melting point being rendered indefinite by conversion into the anhydro-acid now described.

N-Anhydrocarboxymethylaminolauronic Acid,



In order to determine quantitatively the amount of water eliminated by the above fusion, a weighed quantity of carboxymethylaminolauronic acid was heated in a short glass tube at 180 — 190° in a current of carbon dioxide, and the evolved water collected and weighed:

1.1270 lost 0.0882 $H_2O = 7.82$.

$C_{11}H_{19}O_4N$ requires for loss of 1 mol. of water, $H_2O = 7.86$ per cent.

The residue crystallised on cooling in fan-shaped aggregates, which, on recrystallisation from a mixture of benzene and petroleum, melted at 142 — 143° . The compound is readily soluble in water, alcohol ether, acetone, or benzene, sparingly so in petroleum of either low or high boiling point:

Found, $C = 62.3$; $H = 8.15$.

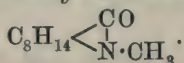
$C_{11}H_{17}O_3N$ requires $C = 62.5$; $H = 8.06$ per cent.

Solvent.—*Water*: $c = 1.465$, $l = 2$, $\alpha - 0.65^{\circ}$, $[\alpha]_D^{19} - 22.2^{\circ}$.

„ *Alcohol*: $c = 1.503$, $l = 2$, $\alpha - 0.35^{\circ}$, $[\alpha]_D^{19} - 11.6^{\circ}$.

„ *Benzene*: $c = 1.239$, $l = 2$, $\alpha - 0.55^{\circ}$, $[\alpha]_D^{19} - 22.2^{\circ}$.

N-Anhydromethylaminolauronic acid,



N-Anhydrocarboxymethylaminolauronic acid (1 mol.) was converted into the barium salt by mixing an aqueous solution with excess of

barium hydroxide (3 mols.) and rapid evaporation to dryness. In this way an intimate mixture of the salt with barium hydroxide was obtained, and this was subjected to distillation in a current of nitrogen. During the process the temperature was gradually raised to 300° . A yellowish-red oil was thus obtained, which gradually solidified to a wax. This substance could not be purified by distillation under diminished pressure, but a sample was obtained for analysis by dissolving in anhydrous ether, filtration, and removal of the solvent on a water-bath. The red, oily residue again gradually solidified, exposure to sunlight deepening the red colour very considerably:

Found, C = 71.5; H = 9.90; N = 8.67.

C = 71.6; H = 10.00; N = 8.36.

$C_{10}H_{17}ON$ requires C = 71.8; H = 10.18; N = 8.38 per cent.

The above constitution of the compound was indicated by the fact that it failed to give a nitrosoamine when acted on with nitrous acid under different conditions. Partial reaction seemed to take place, as the carbon-content of the oily product of the reaction was lowered in different experiments to about 64 per cent. Nitrogen estimations showed, however, that nitrosoamine formation had not taken place, and the result recorded above seems therefore due to oxidation. The above constitution was also supported by the fact that, on heating the compound in a sealed tube with concentrated hydrochloric acid for eight hours at $150-160^{\circ}$, no ammonium chloride was detected in the product.

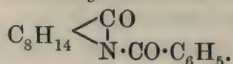
Benzoylaminolauronic acid, $CO_2H \cdot C_8H_{14} \cdot NH \cdot CO \cdot C_6H_5$.

Fifty grams of aminolauronic acid hydrochloride (1 mol.) were dissolved in 300 c.c. of a 10 per cent. solution of sodium hydroxide (3 mols.), and 35 grams of benzoyl chloride (1 mol.) added gradually with constant shaking. When the reaction was complete, the liquid was acidified with hydrochloric acid, the precipitated benzoyl derivative collected, and recrystallised from 80 per cent. alcohol. The compound crystallises in small prisms, melting at 204° . Yield, 60 grams:

Found, C = 69.8; H = 7.59.

$C_{16}H_{21}O_3N$ requires C = 69.8; H = 7.63 per cent.

Solvent.—*Alcohol*: $c = 1.115$, $l = 2$, $a = -0.41^{\circ}$, $[\alpha]_D^{20} = -18.4^{\circ}$.

N-Anhydrobenzoylaminolauronic acid,

With the view of preparing the acid chloride of benzoylaminolauronic acid, 3.5 grams of the latter (1 mol.) were finely powdered, mixed with 20 c.c. of acetyl chloride, and 2.8 grams of phosphorus pentachloride (1 mol.) added. A clear solution was thus obtained. On evaporating off the solvent, an oil remained, which, after distillation at 250°/15 mm., crystallised. Yield, 2.5 grams. On purification by recrystallisation from petroleum of high boiling point, the substance melted at 71—72°. It is readily soluble in alcohol, ether, acetone, or benzene, sparingly so in water or petroleum:

Found, C = 74.7; H = 7.42.

$\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}$ requires C = 74.7; H = 7.40 per cent.

Solvent.—*Alcohol*: $c = 1.476$, $l = 2$, $\alpha - 2.04^\circ$, $[\alpha]_D^{18} - 69.1^\circ$.

Methyl Benzoylaminolauronate, $\text{CO}_2\text{Me} \cdot \text{C}_8\text{H}_{14} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$.

Fifty grams of benzoylaminolauronic acid (1 mol.) were mixed with 110 grams of methyl iodide (4 mols.) and 50 c.c. of pure dry acetone. Ninety grams of dry silver oxide (2 mols.) were added in small quantities from time to time; a vigorous reaction took place, and, after the addition of all the oxide, the mixture was gently boiled for three hours under a condenser. The product was then extracted with boiling ether. The ethereal extract when evaporated to dryness gave a viscid oil, which remained liquid for several months. A specimen dried at 150°/15 mm. crystallised on cooling, and by nucleation the total product was readily obtained in the crystalline state. It was purified by recrystallisation from petroleum of high boiling point. The compound is readily soluble in alcohol, ether, acetone, or benzene, and melts at 88—89°.

Found, C = 70.6; H = 8.06; OMe = 11.3.

$\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$ requires C = 70.6; H = 7.96; OMe = 10.7 per cent.

Solvent.—*Alcohol*: $c = 1.453$, $l = 2$, $\alpha - 0.84^\circ$, $[\alpha]_D^{18} - 28.9^\circ$.

An alcoholic solution of the substance was boiled for three hours with a 10 per cent. solution of sodium hydroxide. As expected, the product of the hydrolysis proved to be the original benzoylaminolauronic acid melting at 204°.

As mentioned in the theoretical part, a saturated solution of ammonia in alcohol was without action on the above ethereal salt, both at the ordinary temperature and at 130°.

I take this opportunity of expressing my indebtedness to the Carnegie Trust for a research grant which defrayed the expenses of the investigation, also to Prof. W. J. Pope, who suggested the research, and to Prof. J. C. Irvine for much valuable advice during the course of the work.

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AND

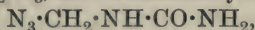
CHEMICAL LABORATORIES,

UNIVERSITY OF CAMBRIDGE.

CXXXIX.—*The Triazo-group. Part XVIII.* *β-Triazoethylamine.*

By MARTIN ONSLOW FORSTER and SIDNEY HERBERT NEWMAN.

AN inquiry into the possibility of producing triazomethylamine (Trans., 1910, **97**, 1056), although unsuccessful so far as the isolation of that base is concerned, led to the discovery that the association of a substituted amino-group with a triazotised carbon atom so weakens the attachment of the azoimide complex that the action of water is sufficient to eliminate hydrazoic acid. Triazomethylcarbimide, $\text{N}_3\cdot\text{CH}_2\cdot\text{N}:\text{C}:\text{O}$, phenyltriazomethylcarbamide, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{N}_3$, and triazomethylcarbamide,



all parted with the triazo-group under the influence of water, thereby explaining the failure of attempts to prepare triazomethylamine from triazoacetamide by Hofmann's reaction.

It was not to be expected, however, that this disability would attend the derivatives of β -triazethylamine, $\text{N}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, although, for another reason, this compound might prove to be unstable. It is well known from the work of Gabriel, that β -halogen substituted ethylamine, salts of which are produced when the respective phthalic derivatives are hydrolysed with hydrochloric and hydrobromic acids, cannot be maintained in the free state on account of their tendency to lose halogen hydride and undergo

transformation into dimethyleneimine, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{NH}$. In view of the general resemblance between the triazo-group and the halogen atoms, therefore, it appeared probable that β -triazethylamine would be realised only in the form of salts, and that these would break up

into metallic azide and dimethyleneimine when treated with alkali. Actual experiment, however, has shown that β -triazoethylamine is a remarkably stable substance. We have isolated it in the form of a colourless liquid, which boils at $63.5^\circ/50$ mm., and may even be distilled from solid potassium hydroxide without undergoing change.

The early attempts to prepare β -triazoethylamine were unsuccessful. Following the lines of Gabriel's experiments in connexion with the corresponding derivatives of ethylamine, bromoethylphthalimide was converted into triazoethylphthalimide, but the temperatures at which this substance undergoes hydrolysis were too high to admit of its application. Triazoethyl iodide was then treated with alcoholic ammonia in the expectation that there would arise a mixture of bases from which the primary one might be isolated; it was found, however, that triazoethylamine derivatives are not produced, the effect of ammonia being similar to that of fixed alkali, namely, removal of hydrogen iodide and liberation of triazoethylene. Ultimately, the simplest possible process was found to be the most applicable; on heating β -bromoethylamine hydrobromide with excess of sodium azide in aqueous alcohol,

$\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HBr} + 2\text{NaN}_3 = 2\text{NaBr} + \text{N}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HN}_3$,
and adding excess of alkali to the liquid, β -triazoethylamine was rapidly carried over by a current of steam. Some typical derivatives of the base have been prepared, but beyond its stability, its properties hardly call for comment, being those of a primary alkylamine; when it is remembered, however, that β -triazopropionic ester behaves towards alkalis exactly like the corresponding halogen derivatives, the tenacity with which the azoimide nucleus is retained in triazoethylamine is noteworthy.

EXPERIMENTAL.

β -Triazoethylamine, $\text{N}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$.

Fifty grams of β -bromoethylamine hydrobromide dissolved in 120 c.c. of water were heated with 36 grams of sodium azide during six hours on the water-bath, when excess of 20 per cent. sodium hydroxide was added, and a current of steam passed through the liquid; the distillate was collected in dilute hydrochloric acid, and yielded about 20 grams of triazoethylamine hydrochloride on evaporation. In order to isolate the base, an aqueous solution of the hydrochloride was saturated with solid potassium hydroxide prior to extraction with ether, it having been found that the latter removes only a very small proportion of the base from a moderately alkaline aqueous solution. On distilling the residue from the

ethereal extract which had remained in contact with solid potassium hydroxide during some days, the triazoethylamine was found still to contain water ($N=63.33$; $C_2H_6N_4$ requires $N=65.09$ per cent.); it was accordingly redistilled from solid potassium hydroxide, boiling steadily at $63.5^\circ/50$ mm.:

0.0884 gave 47.7 c.c. at 14° and 779 mm. $N=65.10$.

$C_2H_6N_4$ requires $N=65.09$ per cent.

β -Triazoethylamine is a colourless, oily liquid, with a marked basic odour, and having $D_{1.0488/16^\circ}$; the effervescence with concentrated sulphuric acid is very vigorous.

Reduction to Ethylenediamine.—The relationship of triazoethylamine to ethylenediamine was established by adding 0.5 gram of the hydrochloride to 50 c.c. of dilute hydrochloric acid in which 0.5 gram of tin foil had been dissolved, agitating the cold solution until gas evolution ceased, and then, having made the liquid alkaline, shaking it with 2 grams of benzoyl chloride, when the product was identified with the dibenzoyl derivative of ethylenediamine.

The *hydrochloride*, prepared in the manner described above, crystallises in colourless, silky needles, melting at 72° :

0.0853 gave 33.8 c.c. N_2 at 18° and 766 mm. $N=46.13$.

0.2710 „ 0.3198 AgCl. $Cl=29.19$.

$C_2H_7N_4Cl$ requires $N=45.74$; $Cl=28.94$ per cent.

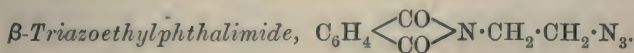
The salt is very hygroscopic, dissolving freely in water and alcohol; it effervesces when thrown into a solution of stannous chloride in hydrochloric acid.

The *benzoyl* derivative was prepared by the Schotten-Baumann process, and remained as a colourless oil, which did not crystallise:

0.1492 gave 38.3 c.c. N_2 at 18° and 759 mm. $N=29.61$.

$C_9H_{10}ON_4$ requires $N=29.47$ per cent.

The substance effervesces vigorously with concentrated sulphuric acid; when heated in alcohol with 30 per cent. sodium hydroxide it is hydrolysed slowly without losing the triazo-group.



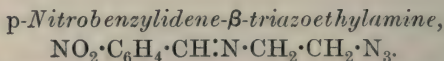
Ten grams of bromoethylphthalimide in 25 c.c. of alcohol were heated with 3.5 grams of sodium azide dissolved in a few c.c. of water during five hours; alcohol was then evaporated, the residue being diluted with water and extracted with ether. The white solid deposited on evaporating the dried ether was recrystallised

from a small quantity of hot alcohol, from which there separated long, pale yellow needles, melting at 58° :

0.0916 gave 20.6 c.c. N_2 at 17° and 763 mm. $N = 26.20$.

$C_{10}H_8O_2N_4$ requires $N = 25.92$ per cent.

Attempts to hydrolyse this material to salts of β -triazoethylamine at moderate temperatures were unsuccessful.

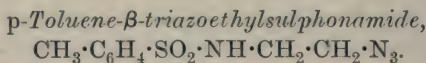


An alcoholic solution of *p*-nitrobenzaldehyde was heated during two hours on the water-bath with the calculated amount of triazoethylamine hydrochloride neutralised with aqueous sodium carbonate; the oil which separated on dilution with water quickly solidified, and was recrystallised from hot petroleum (b. p. $60-80^{\circ}$):

0.0832 gave 22.8 c.c. N_2 at 19° and 777 mm. $N = 32.33$.

$C_9H_9O_2N_5$ requires $N = 31.96$ per cent.

The crystals of this derivative are hard, elongated, rectangular plates, melting at 71° ; they remain transparent in the mother liquor, becoming opaque on exposure to air. The substance is freely soluble in cold acetone, ethyl acetate, chloroform, ethyl alcohol, and benzene. The action with concentrated sulphuric acid is remarkably sluggish, liberation of gas taking place only on prolonged stirring; with stannous chloride and hydrochloric acid there is effervescence on warming.



Molecular proportions of *p*-toluenesulphonyl chloride and of β -triazoethylamine were dissolved separately in ice-cold pyridine, mixed together, and, after two hours, poured into water. The precipitated oil having remained viscous during two days, it was extracted with ether, and shaken with 10 per cent. sodium hydroxide; on saturating the latter with carbon dioxide, a solid was precipitated slowly, and was recrystallised from petroleum:

0.1524 gave 30.8 c.c. N_2 at 17° and 774 mm. $N = 23.89$.

$C_9H_{12}O_2N_4S$ requires $N = 23.35$ per cent.

The sulphonamide dissolves sparingly in hot petroleum, and crystallises in long, slender, lustrous needles, melting at 64° ; it is readily soluble in benzene and in other organic media. The liberation of gas with concentrated sulphuric acid is immediate, but takes place with stannous chloride only on warming.

β -Triazoethylcarbamide, $N_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$.

Two grams of triazoethylamine hydrochloride and 2.6 grams of potassium cyanate were allowed to interact in a few c.c. of water, and left in a vacuum desiccator until dry. The residue was then extracted with absolute alcohol, and the filtered solution of triazoethylcarbamide evaporated to dryness, the final crystallisation being effected by hot benzene, from which it separates in lustrous, snow-white flakes, melting at 59° :

0.0878 gave 40.4 c.c. N_2 at 18° and 779 mm. $N=54.51$.

$C_3H_7ON_5$ requires $N=54.26$ per cent.

The carbamide is insoluble in boiling petroleum, but dissolves very freely in alcohol and in water, these solutions effervescing when heated with stannous chloride.

s-Phenyl- β -triazethylcarbamide, $N_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO \cdot NH \cdot C_6H_5$.

On mixing β -triazethylamine (1 gram) and phenylcarbimide (1.4 gram), both diluted with benzene, the temperature rose, and snow-white needles began to separate after a few minutes; the crystals melted at 99° , and the point of fusion was not raised by recrystallisation from hot benzene:

0.1694 gave 0.3274 CO_2 and 0.0874 H_2O . $C=52.71$; $H=5.64$.

$C_9H_{11}ON_5$ requires $C=52.68$; $H=5.36$ per cent.

The substance dissolves readily in cold ethyl alcohol, ethyl acetate, chloroform, or hot benzene, but is sparingly soluble in boiling water or petroleum. Evolution of gas with concentrated sulphuric acid is very vigorous, but with stannous chloride takes place only when the liquid is heated.

s-Phenyl- β -triazethylthiocarbamide, $N_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CS \cdot NH \cdot C_6H_5$.

Although heat was developed on mixing triazoethylamine and phenylthiocarbimide in benzene solution, the product did not crystallise until sown:

0.1348 gave 36.0 c.c. N_2 at 15° and 776 mm. $N=31.95$.

$C_9H_{11}N_5S$ requires $N=31.69$ per cent.

The thiocarbamide dissolves sparingly in boiling water or petroleum, crystallising from the latter in long, narrow, rhomboidal plates, melting at 64° ; it is freely soluble in cold methyl alcohol, ethyl acetate, chloroform, acetone, and benzene.

β-Triazoethylquinolinium Iodide, $C_9H_7N \begin{smallmatrix} < CH_2 \cdot CH_2 \cdot N_3 \\ I \end{smallmatrix}$.

Five grams of triazoethyl iodide and 3.2 grams of quinoline were mixed in a stoppered bottle and left in darkness; crystals began to separate in the course of a few days, and amounted to two grams at the end of three weeks, whilst a further quantity was deposited subsequently. The salt is readily soluble in hot alcohol, crystallising in transparent, golden-yellow prisms; it becomes suddenly deep red at 162° , and melts and decomposes at $162\text{--}164^\circ$:

0.2164 gave 32.0 c.c. N_2 at 18° and 759 mm. $N=17.06$.

0.2232 „ 0.1586 AgI. $I=38.42$.

$C_{11}H_{11}N_4I$ requires $N=17.18$; $I=38.94$ per cent.

In order to convert the quinolinium iodide into the platinum-chloride, an alcoholic solution was shaken with freshly precipitated silver chloride; it became colourless, and after filtration was treated with slight excess of platinic chloride, which gave a pale red precipitate:

0.1292 gave 15.6 c.c. N_2 at 19° and 745 mm. $N=13.63$.

0.1464 „ 0.0356 Pt. $Pt=24.31$.

$C_{22}H_{22}N_8Cl_6Pt$ requires $N=13.79$; $Pt=24.18$ per cent.

The *platinichloride* is insoluble in boiling alcohol, and requires a considerable proportion of boiling water for dissolution, separating in long, flat, pale brown needles; these melt with vigorous intumescence at 200° .

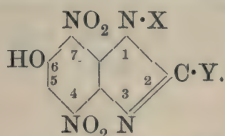
Attempts to prepare similar salts from methylaniline and dimethylaniline were unsuccessful, and the action of piperidine was found to resemble that of ammonia, causing a rapid separation of piperidine hydriodide.

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CXL.—*Syntheses with Phenol Derivatives Containing a Mobile Nitro-group. Part IV. Quinone-imides; Asymmetric Quaternary Ammonium Compounds and Asymmetric Carbinols.*

By RAPHAEL MELDOLA and HAROLD KUNTZEN.

THE iminazoles described in previous communications to the Society as resulting from the condensation of 2:3:5-trinitro-4-acetylaminophenol with primary amines may be formulated:

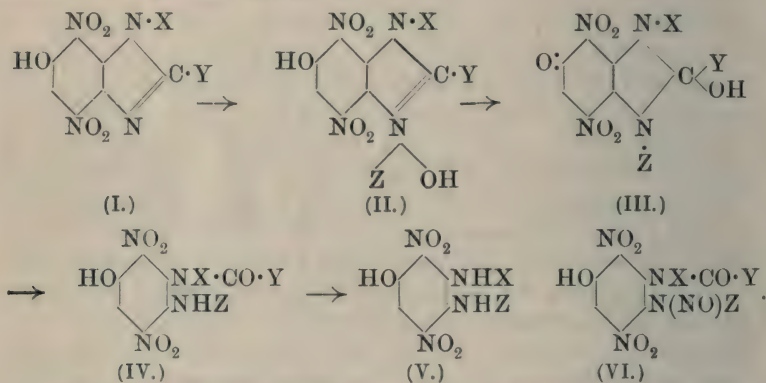


From this formula it will be seen that the radicles X and Y are completely under control, X representing the radicle contained in the primary amine, and Y that contained in the acid radicle of the 4-acylamino-group of the original trinitrophenol derivative. In all the iminazoles hitherto described, Y has represented CH_3 , since the trinitro-compound contained the acetyl group. New iminazoles of the above type, in which Y represents C_3H_7 and C_4H_9 , prepared from the corresponding propionyl and valeryl derivatives of the trinitroaminophenol, are now under investigation.

The extreme stability of these iminazoles, combined with their marked acid (phenolic) character, suggested the possibility of their being convertible into amines or diamines containing an acid radicle, a class of compounds of special interest in connexion with the stereochemistry of nitrogen (Trans., 1910, **97**, 446). As a preliminary to the preparation of such compounds, the iminazole ring would have to be broken down, a problem which might have been expected to present considerable practical difficulties in view of the well-known stability of this ring. No method of reduction likely to affect the nitro-groups would have been of use in the present case. Of other known methods of breaking down the iminazole ring, the most direct is that of Bamberger and Berlé (*Annalen*, 1893, **273**, 343), who found that with certain iminazoles benzoyl derivatives of the ortho-diamines were formed by the action of benzoyl chloride in the presence of alkali (Schotten-Baumann method). With the iminazoles prepared from trinitroacetylaminophenol, however, this method fails, the strongly acid character of the phenolic nucleus giving such stability to the iminazole ring that

benzoyl chloride and alkali fail to bring about the rupture of the latter. In most of our compounds, moreover, the 6-hydroxyl group is so effectively protected by the adjacent 7-nitro-group that even ordinary benzoylation does not take place. The stability of the iminazole ring in presence of benzoyl chloride and alkali has been observed in other cases (Niementowski, *Ber.*, 1899, **32**, 1460).

Another method of passing from iminazoles to symmetrical substituted orthodiamines is due to Otto Fischer, who found that N^1N^3 -dialkylated iminazoles could be broken down by hydrolysis. The study of this reaction has engaged the attention of this author and his colleagues for many years (*Ber.*, 1899, **32**, 1312, and subsequent papers; *J. pr. Chem.*, 1906, [ii], **73**, 419; 1906, **74**, 57; 1907, **75**, 88 *). The mechanism of this decomposition, if such occurred in the series now under investigation, would, according to Fischer's results, be expressed by the formulæ:



The hypothesis that the ammonium hydroxide form (II) is capable of assuming the tautomeric carbinol form (III) is due to Niementowski (*Ber.*, 1887, **20**, 1887, also Pinnow and Saemann, *Ber.*, 1899, **32**, 2182), and is amply supported by the later experiments of O. Fischer. As will be seen from the experiments described in the present paper, the breaking down of the iminazole ring by O. Fischer's method has also failed. Under no conditions have we

* In this last paper O. Fischer has shown that the apparent isomerism of certain iminazoles (aminoamidines) of the naphthalene series observed by the author and his colleagues (*Trans.*, 1899, **75**, 1011; 1900, **77**, 1159; 1903, **83**, 1185; 1904, **85**, 1592) is due to the circumstance that one set of the compounds investigated by us belongs to the series of "oxyanhydro-bases" of Niementowski (*Ber.*, 1887, **20**, 1875; 1892, **25**, 862, and subsequent papers). The discrepancies between different investigators in this group of compounds are no doubt due to the extreme mobility of the oxygen atom in the oxyiminazole ring, and the readiness with which this passes into the iminazole ring (see Niementowski's last paper, *Ber.*, 1910, **43** 3016; also the author in *Proc.*, 1911, **27**, 98).—R. M.

as yet been able to realise stages IV and V of the above scheme, the alkylated iminazole resisting the action of alcoholic or aqueous alkali altogether or undergoing complete decomposition under extreme conditions, with the formation of isocyanides and indefinite resinous products. Acid hydrolysing agents also fail to break down the iminazole ring. This result is the more remarkable since Fischer has found that with chloro- and chloronitro-benziminazoles the iminazole ring is more easily ruptured than in the case of the iminazoles not containing acid radicles in the benzene nucleus (*J. pr. Chem.*, 1906, [ii], **74**, 57). It appears that the weakening influence of the acid radicles in the case of the simpler iminazoles is compensated for in our iminazoles by the special influence of the hydroxyl group, which introduces a new set of conditions and leads to the display of very remarkable properties on the part of these compounds.

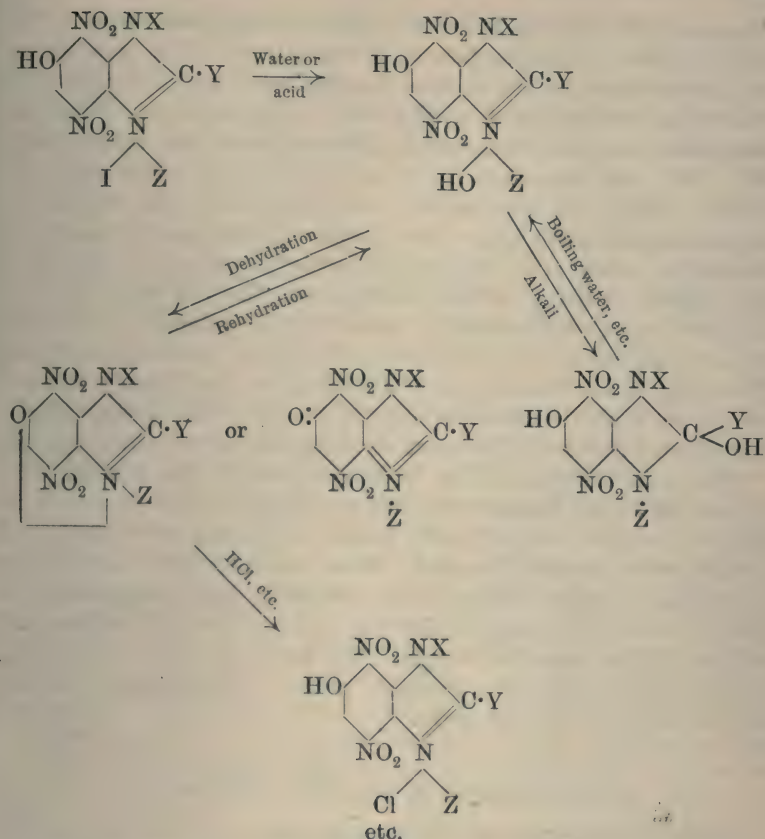
The temporary resolution of the iminazole ring by means of nitrous acid observed by O. Fischer (*J. pr. Chem.*, 1906, [ii], **73**, 423) has also proved to be inapplicable in the case of the iminazoles investigated by us. Had this resolution been possible with our compounds, nitroso-amines of the general formula No. VI (above) might have been synthesised. Nitroso-amines of this type are, however, according to Fischer's observations, incapable of being converted into orthodiamine derivatives, as the removal of the nitroso-group by means of acids leads at once to ring formation and the reproduction of the original iminazole. With the iminazoles described in this paper, no formation of nitroso-amines takes place, although in some instances a temporary and very unstable combination with nitrous acid has been observed, but the product decomposes on mere exposure to the air, with the regeneration of the original iminazolium base. As these compounds are too unstable for isolation, we have no evidence that they are actually nitroso-amines; it is most probable that they are unstable nitrites of the ammonium base (No. II).

Interconvertibility of Ammonium Compounds and Carbinols.

The increased stability of the iminazoles resulting from the presence of the hydroxyl and nitro-groups in the benzene nucleus has enabled us to obtain very definite evidence with respect to the conditions determining the configuration in these pairs of isomerides. In every case the three isomerides Nos. II, III, and IV are theoretically possible. As already stated, our iminazoles, when alkylated and decomposed by water, alkali, or acid, fail to yield any compound of the type No. IV. The decision between II and

III is based on the observation that one set of compounds is distinctly basic, yielding well defined salts with acids, whilst the isomeric set is non-basic and distinctly phenolic in character. The basic compounds we therefore regard as ammonium derivatives (No. II), and the phenolic compounds as carbinols (No. III). This conclusion is supported by the discovery that the former (No. II) readily lose a molecule of water, and give rise to a new type of quinone-imide derivatives (see below), while the latter (No. III) cannot be dehydrated. The ammonium bases are easily convertible into the carbinols by the action of alkali. It is only necessary to dissolve these compounds in hot dilute alkali, and to precipitate by acid, when the carbinol separates from the solution as an ochreous, micro-crystalline, insoluble deposit. On the other hand, the carbinols, on boiling with water or dilute alcohol, gradually pass into solution, and are converted into the ammonium compounds, which crystallise out on cooling. In all the cases hitherto studied, with one exception, there is a marked difference in colour between the two forms, the ammonium compound and corresponding quinone-imide being bright red and the carbinol light ochreous. This difference in colour between the isomerides has enabled us to follow the transformation with facility. The exceptional case referred to is when X in the above formulæ (II and III) stands for *p*-tolyl, the other radicles, Y and Z, being methyl. In this compound both forms are similar in colour (ochreous), a case of special interest in connexion with theories of the relationship between colour and chemical constitution. It may be regarded as certain that this compound has the same constitution as the corresponding dimethyl-iminazoles, in which X stands for phenyl *p*-chlorophenyl or *p*-anisyl. The latter in their ammonium forms are bright red, while the tolyl ammonium compound is light ochreous. A case of this kind emphasises the necessity for exercising caution in pushing to an extreme theories of constitution based only on the visual colour of organic compounds.

The relationship between the iminazoles, quinone-imides, and carbinols is shown in the subjoined scheme:



Alkylation of the Iminazoles.

The accumulation of acid radicles, and especially the presence of the hydroxyl group in the benzene nucleus, has the general effect of weakening the capacity of the 3-N-atom of the iminazole ring for attaching alkyl iodides. The iminazoles synthesised by means of trinitroacetylaminophenol, so far as we have at present investigated them, can only be converted into their alkyl iodides by heating them to a high temperature (about 120—130°) with excess of undiluted alkyl iodide. Methyl iodide has been used in most of the experiments described in this paper, so that Z in the above formulæ represents CH₃. In one case Z represents C₂H₅, and the experience gained with this compound (X=phenyl; Y=methyl; Z=ethyl) points to the conclusion that the difficulty of alkylation

increases with the weight of the radicle represented by Z. This point, however, requires further investigation. The presence of acid substituents in the radicle X attached to the 1-N-atom also checks the attachment of alkyl iodide to the 3-N-atom. Thus the iminazoles from the chloroanilines (Meldola and Hay, *Trans.*, 1908, **93**, 1667) are alkylated less readily than those prepared from aniline. With the nitroaniline and sulphanilic acid iminazoles, negative results have so far been obtained. The general properties referred to relate only to those iminazoles in which X represents an aromatic radicle; in these compounds the 1-N-atom has not hitherto been found capable of assuming the quinquivalent form. In one case, however, in which the ethylamine iminazole was used ($X = C_2H_5$) it was found that a dimethiodide was readily formed, so that an aliphatic radicle appears to facilitate the further alkylation of the 1-N-atom. This point also requires further investigation.

The special influence of the hydroxyl group in the benzene ring is most strikingly shown when the alkylation is carried out, as in most of the cases studied by O. Fischer, by means of a solution of methyl iodide in methyl alcohol. When this mixture is used, either no alkylation takes place or, at a sufficiently high temperature, a tarry product is formed, which on opening the tube decomposes with a copious evolution of gas. We have not yet followed out this reaction, as the tarry products are very unpromising, but the subject will be taken up again.

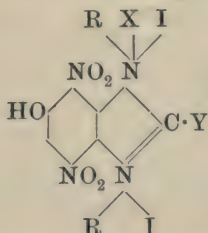
Decomposition of the Alkyl Halides.

In the present series of experiments methyl (in one case ethyl) iodide was used, so that the initial product is, with the one exception, the methiodide. The influence of halogens other than iodine has yet to be investigated. The methiodides are easily decomposable, either by boiling with water or in some cases with dilute hydrochloric acid, the acid extract being afterwards neutralised by ammonia. In all cases the ammonium compound crystallises out as the solution cools. Owing to the instability of the methiodides in the presence of hydrolysing solvents they cannot be purified by crystallisation, so that the products are dealt with directly as they come from the tube, the crystalline methiodides being but sparingly soluble in cold alcohol, and therefore sufficiently purifiable by washing with this solvent, which removes excess of methyl iodide. The ammonium hydroxide base having been isolated by the above method, is convertible into other salts (chloride, bromide, etc.) by the action of various acids. All these salts are much more soluble in water than the iodides, and are hydrolysed by excess of the

solvent, so that special methods, which are described in the experimental part of the paper, have had to be adopted for their isolation. The methiodides are also decomposed rapidly by alkali, even in the cold, but the products in this case, when precipitated from the alkaline solution by acid, consist of the carbinol (see the scheme given above).

The Asymmetry of the Ammonium Compounds and Carbinols.

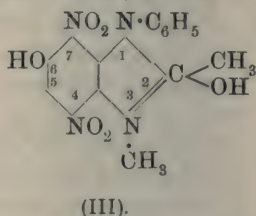
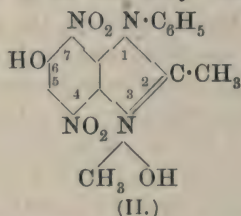
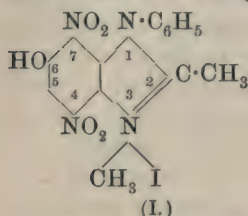
It will be seen from the formulæ in the foregoing scheme that the 3-N-atom in the ammonium compounds is in the condition of asymmetry represented by compounds of the type $O:Nabc$, which have been shown by Meisenheimer to be possessed of optical activity (*Ber.*, 1908, **41**, 3966). The corresponding carbinols are also obviously asymmetric, and as they are directly obtainable from their ammonium isomerides, we have here the interesting possibility of being able to resolve a compound containing an asymmetric nitrogen atom, and then transferring the asymmetry from the nitrogen to the carbinol carbon atom. This part of the research will be entered upon as soon as possible, and we only call attention to the matter now in a preliminary way in order to indicate the proposed line of investigation. The possibility of obtaining such optically active and interconvertible isomerides is, of course, dependent, apart from the question of practicability, upon the correctness of the constitution which we have assigned to the compounds; the optical evidence, if obtainable, may enable us to test the validity of the formulæ proposed. We may point out, further, that in the case of iminazoles containing a fatty radicle in position I, compounds of the type:



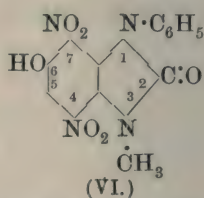
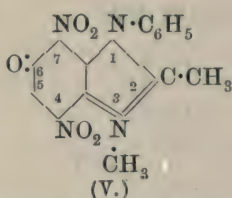
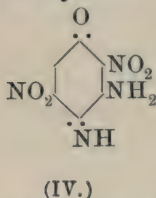
appear to be easily formed. These dialkyl iodides are of special interest as containing two asymmetric nitrogen atoms, and it is proposed to continue their investigation.

Nomenclature.

As two new classes of compounds come under consideration in the present paper, and as the nomenclature requires systematising for purposes of reference, it appears desirable to adopt some definite scheme for future use in dealing with these compounds. Since the latter are derivatives of benziminazole, the nomenclature adopted in former papers for these compounds only requires a little modification to adapt it to the alkyl halides. Thus, I and II



would be written 4:7-dinitro-6-hydroxy-1-phenyl-2:3-dimethylbenziminazolium iodide and hydroxide respectively. For the carbinols, the general designation "iminazolol" used by O. Fischer and others may usefully be adopted for the present series. Thus III would be 4:7-dinitro-6-hydroxy-1-phenyl-2:3-dimethyl-2-benziminazolol. The quinone-imides may be regarded as derivatives of the hypothetical dinitroaminoquinoneimide (IV), and it is proposed to name these compounds "iminazolones," a designation equally applicable to the products which might be expected to result from the oxidation of the iminazolols (Pinnow and Saemann, *Ber.*, 1899, **32**, 2191).^{*} The formulæ given below will illustrate the application of the proposed system :



V would be 4:7-dinitro-1-phenyl-2:3-dimethyl-6-benziminazolone; VI would be 4:7-dinitro-6-hydroxy-1-phenyl-3-methyl-2-benziminazolone.

EXPERIMENTAL.

4:7-Dinitro-6-hydroxy-1-phenyl-2:3-dimethylbenziminazolium Iodide.

This compound (No. I formula above) was prepared by heating the corresponding iminazole (Trans., 1906, **89**, 1939) with excess of

^{*} The products of oxidation are under investigation.

methyl iodide in a sealed tube for twelve hours at 130°. The product, after being removed from the tube and washed with cold alcohol and dried, consisted of a dense, red, ochreous, crystalline powder, having a decomposing point of about 242—244°. For the reasons stated in the introductory section it could not be crystallised from any solvent, but analysis indicated that the methylation was practically complete:

0.1025 gave 11.65 c.c. N₂ (moist) at 18° and 763.1 mm. N=12.52.

0.0941 „ 0.0470 AgI. I=26.86. (Determined by decomposing the compound suspended in hot alcohol with a solution of silver nitrate.)

C₁₅H₁₃O₅N₄I requires N=12.28; I=27.83 per cent.

Numerous experiments were made with this methiodide with the object of discovering the most suitable method for hydrolysing it so as to obtain a definite product. The special properties of the ammonium hydroxide base introduced unexpected difficulties, which had to be overcome before any conclusion respecting its formula could be based on the analytical results.

4:7-Dinitro-6-hydroxy-1-phenyl-2:3-dimethylbenziminazolum Hydroxide.

The above methiodide was boiled for about an hour with a large volume of water until it had practically all passed into solution, and the latter, after filtration, when cold deposited flat, red needles of the ammonium hydroxide compound. At this stage the product, as shown by analysis and qualitative tests, is apt to contain more or less undecomposed methiodide, as the latter is to some extent soluble in the solution of its product of decomposition, and crystallises out therewith on cooling. The aqueous treatment had therefore to be repeated until the product was free from iodine, two extractions with boiling water being generally found sufficient to insure the deposition of a pure compound. The latter, when allowed to dry in the air, consists of flat, red needles, which become much deeper in colour on drying in the water-oven. The decomposing point is about 283—285°, but this is really the decomposing point of the iminazolone, as complete dehydration takes place much below this temperature.

The first complication that arose in the course of our study of this compound was the want of concordance among the analytical results as given by specimens dried under various conditions. It was found that the substance, when dried in the oven at 100° until constant in weight, regained weight rapidly during the process of weighing, hydration by atmospheric moisture being thereby indicated. This hydration is accompanied by a change in colour, the

deep red becoming lighter and more orange in shade. Omitting details of the numerous experiments and analyses, the general results show that when air-dried at the ordinary temperature the substance contains one molecule of "attached" water. Dried at 100° the loss corresponds with two molecules of water, indicating the loss of the "attached" molecule, and also of the molecule eliminated by the dehydration of the ammonium hydroxide derivative. When this point is reached, no further loss takes place at 110 — 120° , and the substance, then deep red in colour, is the quinone-imide (iminazolone). Even at the ordinary temperature in a desiccator containing calcium chloride the compound undergoes complete dehydration, and passes into the quinone-imide in the course of two or three days. Some of the analytical results by which these changes have been followed are now given:

0.1031, dried at 100° , gave 15.5 c.c. N_2 (moist) at 18° and 753.2 mm. $N=17.20$.

0.0750, dried at 110° , gave 11.15 c.c. N_2 (moist) at 18° and 763 mm. $N=17.20$.

0.1437, dried at 100° , gave 0.2873 CO_2 and 0.0488 H_2O . $C=54.62$; $H=3.77$.

0.1030 (dried at 100° , and then exposed to the air until constant in weight) gave 14.05 c.c. N_2 (moist) at 18.5° and 750 mm. $N=15.5$.

0.1104 (same as above) gave 0.1994 CO_2 and 0.0440 H_2O . $C=49.26$; $H=4.44$.

0.5004 (air-dried) lost, at 100° , 0.0496 $H_2O=9.9$ per cent.

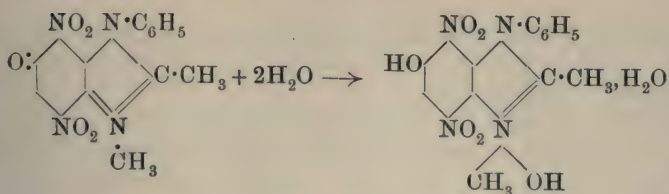
The iminazolone, $C_{15}H_{12}O_5N_4$, requires $C=54.85$; $H=3.68$; $N=17.08$ per cent.

The ammonium hydroxide form, $C_{15}H_{14}O_6N_4$, requires $C=52.0$; $H=4.07$; $N=16.18$ per cent.

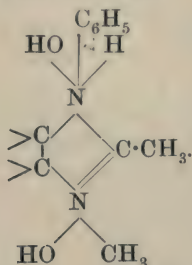
The above hydrate, $C_{15}H_{14}O_6N_4 \cdot H_2O$, requires $C=49.42$; $H=4.42$; $N=15.39$ per cent.

$C_{15}H_{14}O_6N_4 \cdot H_2O - 2H_2O$ requires a loss = 9.89 per cent.

The question of the constitution of the hydrated product has been considered, but the evidence at present does not appear to warrant any definite decision. The point to be decided is whether the one molecule of water which at first attached itself converts the quinonoid compound into the ammonium hydroxide form, or whether it is simply "molecularly" combined, as is apparently the case with the second molecule:



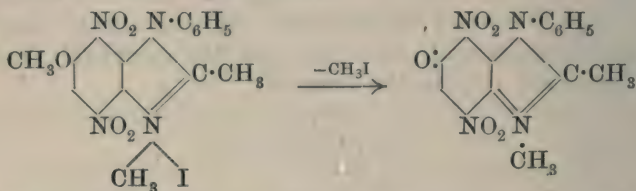
The red colour of the quinone-imide and its product of hydration might be urged in favour of the quinonoid structure of both, in which case the two molecules of water would be "molecularly" combined. The argument from colour, however, as already pointed out in the introductory section, fails in this case because the corresponding iminazolone containing *p*-tolyl in place of phenyl is of an ochreous colour similar to that of the isomeric carbinols. An attempt was made to obtain direct evidence on this point by observing the rate of dehydration and rehydration. Supposing the two molecules to be differently combined, it was thought possible that the curves of hydration and dehydration might show a break at the point when one molecule of water is lost on drying or regained on exposing the anhydrous compound to the air. A dried specimen was therefore exposed, and weighed at regular intervals, the weights and times being taken as ordinates and abscissæ, and the curve constructed from the points thus given. We have not thought it necessary to reproduce the curves, but the observations indicate that the hydration is uniform, and that no break occurs at the critical point corresponding with one H_2O . All that can be deduced from this result is that the two molecules may, but not necessarily must, be attached in the same kind of way, but it does not follow that the original monohydrate must be quinonoid, because the 1-N-atom of the iminazole ring may also be capable of becoming quinquevalent, in which case the completely hydrated compound would contain the complex:



It is of interest to place on record the fact that no other of the iminazolium compounds which we have hitherto prepared contains attached water. The extreme stability of this iminazolium hydroxide

is shown by its behaviour towards concentrated sulphuric acid, with which it can be heated to the fuming point of the latter without undergoing decomposition.

In connexion with the relationship between colour and constitution, it appeared of importance to prepare, if possible, an iminazolium hydroxide in which the quinonoid structure was made impossible by the substitution of an alkyloxy-group for the para-hydroxyl group. The alkyl ethers of the iminazoles can be prepared by the action of alkyl iodides on the silver salts (Meldola and Hay, *Trans.*, 1908, **93**, 1672), and the iminazolium hydroxides from these would fulfil the necessary conditions. Experiments with the methyl and ethyl ethers of the iminazole indicated, however, that the desired compounds could not be prepared owing to the remarkable facility with which the alkyloxy-group becomes dealkylated. The results, although negative from the point of view which prompted the experiments, are in themselves of interest. The methyl ether (m. p. 205–206°) when heated with excess of methyl iodide at 130° yields a product consisting of a mixture of the unchanged compound and the ordinary (demethylated) iminazolium iodide. At 150° complete demethylation takes place. The ethyl ether heated with excess of methyl iodide at 115° gave a product which apparently contained a small quantity of the methiodide, but this, on conversion into the iminazolium hydroxide by the usual method, again gave the ordinary (dealkylated) compound, indicating that the ethyl group had also been eliminated either before or during the process of hydrolysis. Dealkylation by means of methyl iodide is not often observed; in the present case the mechanism of the process may be thus represented:



4:7-Dinitro-6-ethoxy-1-phenyl-2-methylbenziminazole, which had not hitherto been described, crystallises from alcohol in flat, ochreous needles, melting sharply at 179°:

0.1683 gave 23.9 c.c. N_2 (moist) at 17.5° and 761.4 mm.
 $\text{N} = 16.43$.

$\text{C}_{16}\text{H}_{14}\text{O}_5\text{N}_4$ requires $\text{N} = 16.41$ per cent.

4:7-Dinitro-6-hydroxy-1-phenyl-2:3-dimethylbenziminazolol.

The red iminazolium hydroxide or the corresponding iminazolone dissolves slowly in dilute sodium hydroxide solution at the ordinary temperature, and more rapidly on heating, with the formation of an orange-coloured solution, which contains the sodium salt of the above carbinol. The latter is precipitated by the addition of acid as an ochreous, micro-crystalline powder, insoluble in cold alcohol or water. The compound when dried in the air is anhydrous, and undergoes no loss of weight on heating. The decomposing point is about the same as that of the isomeric ammonium compound ($281-283^{\circ}$), and we have reason to believe that at the temperature of decomposition the latter is really formed by isomeric change, and that the decomposing point is really that of the iminazolone:

0.0868 gave 0.1688 CO_2 and 0.0334 H_2O . $\text{C}=52.03$; $\text{H}=4.27$.

0.1244 „ 17.7 c.c. N_2 (moist) at 19° and 754.5 mm. $\text{N}=16.24$.

$\text{C}_{15}\text{H}_{14}\text{O}_6\text{N}_4$ requires $\text{C}=52.0$; $\text{H}=4.07$; $\text{N}=16.18$ per cent.

The action of various reagents on the carbinol has been studied with the object of obtaining confirmatory evidence respecting its constitution, but no definite derivatives have been obtained. Heating in a sealed tube with hydrochloric acid at 130° converts it into the ammonium form; so also does methyl iodide at 150° , and phosphorus pentachloride at the ordinary temperature. When heated with the latter, carbonisation takes place. Highly oxidisable products are formed by the partial or complete reduction of the compound. No methylation takes place with methyl sulphate and alkali; benzoyl chloride and alkali give resinous products. Aqueous and alcoholic solutions of potassium hydroxide of various strengths were tried, but no decomposition took place if the solution was too weak, and with a 33 per cent. solution complete decomposition, with the production of isocyanide, resulted. The carbinol is non-basic and distinctly phenolic, but not acid enough to form salts with alkaloids. It was hoped that resolution might be effected by means of brucine, but the only effect of heating the substance with an alcoholic solution of the alkaloid is to convert it into the ammonium base. These experiments will, however, be continued with other alkaloids.

The general properties of the carbinol clearly indicate that under ordinary conditions the iminazolium configuration is the more stable. This is shown by the ready conversion into the latter by prolonged boiling with water or, better, with dilute alcohol. The above-described experiments show generally that the action of heat is to bring about the transformation, and confirmatory evidence is given in the next section dealing with the salts.

Iminazolium Salts.

The replacement of the ammonium hydroxyl group by acid radicles readily takes place when the red hydroxide (or quinone-imide) is dissolved in dilute acids. The salts are, to the eye, colourless in solution and white in the solid state.* They are more or less dissociable by water, exchanging the acid radicle for hydroxyl, and passing back to the ammonium form; for this reason the isolation of definite salts has presented considerable practical difficulties. Thus the iodide and bromide prepared by dissolving the base in aqueous or alcoholic hydriodic or hydrobromic acid gave results on analysis which indicated that some unconverted or dissociated base was always present.

4 : 7-Dinitro-6-hydroxy-1-phenyl - 2 : 3 - dimethylbenziminazolium chloride was prepared by adding the base to a cold saturated solution of hydrogen chloride in absolute alcohol. Both the ammonium and quinone-imide forms give the same product, which consists of white, microscopic needles. The latter, dried by exposure to the air, were analysed:

0.30 gave 0.1213 AgCl. Cl=9.99.

0.3196 „ 0.1290 AgCl. Cl=9.97.

0.1732 „ 22.15 c.c. N₂ (moist) at 17° and 773 mm. N=15.24.

C₁₅H₁₃O₅N₄Cl requires Cl=9.72; N=15.34 per cent.

The salt is rapidly decomposed by boiling water, with the regeneration of the red ammonium base.

Platinichloride.—An aqueous solution of the chloride gives an immediate precipitate of a light ochreous colour on being mixed with a solution of platinic chloride. This precipitate, on being collected and washed with water, showed signs of dissociation with the formation of an orange-coloured salt. When dried by exposure to the air, the two compounds were easily separable; the coloured product was present only in small quantity, and was not analysed. The main ochreous precipitate, which was amorphous, and a further deposit from the mother liquor which separated in the form of ochreous, crystalline plates, consisted of the platinichloride:

0.0170 (main precipitate air-dried) gave 0.003 Pt=17.64 per cent.

0.0484 (ochreous plates from mother liquor air dried) gave 0.0085 Pt=17.56 per cent.

0.0391 (ochreous plates) gave 3.5 c.c. N₂ (moist) at 16° and 755 mm. N=10.31.

(C₁₅H₁₃O₅N₄Cl)₂.PtCl₄.2H₂O requires Pt=17.7; N=10.2 per cent.

* The iodide prepared as above or by direct methylation of the iminazole is ochreous, but it is possible that it has not yet been obtained quite free from ammonium base. The pure salt, if obtainable, may be white.

The *ferrichloride* is precipitated in microscopic, light ochreous needles on mixing strong solutions of ferric chloride and the iminazolium chloride. The salt is readily soluble in cold water, but less so in alcoholic hydrochloric acid:

0.0306 gave 0.0047 Fe_2O_3 . $\text{Fe}=10.75$.

0.0475 „ 4.5 c.c. N_2 (moist) at 18° and 763.8 mm. $\text{N}=10.95$.

$\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}_4\text{Cl}\cdot\text{FeCl}_3$ requires $\text{Fe}=10.62$; $\text{N}=10.63$ per cent.

Nitrate.—The ammonium base dissolves in boiling dilute nitric acid, and the solution on cooling deposits the salt in dense, white prisms, which become ochreous on drying in the air or under a desiccator:

0.1063 gave 15.7 c.c. N_2 (moist) at 12° and 762.2 mm. $\text{N}=17.58$.

$\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}_4\cdot\text{NO}_3$ requires $\text{N}=17.65$ per cent.

The salt on prolonged drying over lime in a desiccator, and more rapidly on drying at 100° , becomes reddened, and loses nitrogen, thus indicating elimination of nitric acid and transformation into the iminazolone. Specimens dried under a desiccator for three weeks were found to contain 17.15 and 17.01 per cent. of nitrogen.

Of the organic salts, the acetate is the only one that has been isolated. A resinous picrate is formed on boiling an alcoholic solution of the base with picric acid and allowing the solution to cool; this salt dissociates on boiling with alcohol, and could not be obtained as a definite compound.

Acetate.—This salt is readily formed on boiling the ammonium base with glacial acetic acid, from which it separates on cooling in golden scales, decomposing at about $286\text{--}287^\circ$, which is probably the decomposing point of the dissociated salt. The same salt is formed when the carbinol is boiled with glacial acetic acid, another instance of the ready transformation of the latter into the more stable form being thus furnished. The salt is easily dissociated by water, and also shows signs of dissociation on heating in the water-oven:

0.1900 gave 0.3644 CO_2 and 0.0672 H_2O . $\text{C}=52.30$; $\text{H}=3.93$.

0.1546 „ 0.3057 CO_2 „ 0.0562 H_2O . $\text{C}=52.46$; $\text{H}=3.91$.

0.1193 (air-dried) gave 14.7 c.c. N_2 (moist) at 16° and 753.6 mm.

$\text{N}=14.22$.

0.1030 (air-dried) gave 12.8 c.c. N_2 (moist) at 17° and 754.9 mm.

$\text{N}=14.41$.

$\text{C}_{17}\text{H}_{16}\text{O}_7\text{N}_4$ requires $\text{C}=52.22$; $\text{H}=4.14$; $\text{N}=14.43$ per cent.

4 : 7-Dinitro-6-hydroxy-1-phenyl-2-methyl-3-ethylbenziminazolium
Hydroxide.

As the iminazole is never completely converted into its ethiodide, no attempt was made to isolate the latter, but the whole product

obtained by heating the iminazole with ethyl iodide at 130° for four hours, after the usual treatment, was extracted with boiling water, and the filtered solution allowed to cool. The crystalline deposit was collected, and recrystallised from boiling water, the iminazolium hydroxide being thus obtained in bright red, flat needles, having a decomposing point of about 250 — 258° . The air-dried substance is not completely dehydrated at 100° , but requires a temperature of 110° in order to convert it into the iminazolone:

0.1242 (air-dried) gave 0.2417 CO_2 and 0.0533 H_2O . $\text{C}=53.07$; $\text{H}=4.76$.

0.0976 (air-dried) gave 13.15 c.c. N_2 (moist) at 16.5° and 751.4 mm. $\text{N}=15.61$.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_4$ requires $\text{C}=53.3$; $\text{H}=4.48$; $\text{N}=15.55$ per cent.

4:7-Dinitro-6-hydroxy-1-phenyl-2-methyl-3-ethylbenziminazolone.

Prepared by heating the foregoing compound to 110° until constant in weight; the substance does not differ in appearance from the iminazolium hydroxide:

0.1106 gave 0.2271 CO_2 and 0.0432 H_2O . $\text{C}=56.0$; $\text{H}=4.34$.

0.0918 „ 12.8 c.c. N_2 (moist) at 14.5° and 764.5 mm. $\text{N}=16.46$.

0.5231 iminazolium hydroxide (air-dried) lost at 110° 0.0260 = 5 per cent.

$\text{C}_{16}\text{H}_{14}\text{O}_5\text{N}_4$ requires $\text{C}=56.12$; $\text{H}=4.12$; $\text{N}=16.37$ per cent.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_4\text{H}_2\text{O}$ requires a loss = 5 per cent.

Iminazolium Salts.

The red iminazolium hydroxide is at once precipitated as a white chloride on adding it to an alcoholic solution of hydrogen chloride and diluting with ether. The product, as shown by analysis, consists of a mixture of the mono- and di-chlorides, so that an additional molecule of hydrogen chloride is attached, most probably to the 1-N-atom. (Found, $\text{N}=13.52$; $\text{Cl}=11.83$. Calc., for monochloride, $\text{N}=14.8$; $\text{Cl}=9.36$; for dichloride, $\text{N}=13.5$; $\text{Cl}=17.08$ per cent.)

4:7-Dinitro-6-hydroxy-1-phenyl-2-methyl-3-ethylbenziminazolium iodide, prepared by adding concentrated aqueous hydriodic acid to the iminazolium hydroxide suspended in absolute alcohol, crystallises in small, red, ochreous needles:

0.1150 gave 0.0565 $\text{AgI} = 26.6$ I.

0.0890 „ 8.9 c.c. N_2 (moist) at 19° and 764.3 mm. $\text{N}=11.55$.

$\text{C}_{16}\text{H}_{15}\text{O}_5\text{N}_4\text{I}$ requires $\text{I}=27.05$; $\text{N}=11.91$ per cent.

The salt used for analysis was air dried, and the iodine determined in the wet way by decomposing the iodide with silver nitrate in presence of excess of dilute nitric acid.

The *platinichloride* is precipitated as an ochreous, amorphous substance on adding a solution of platinic chloride to a solution of the iminazolium chloride. The analyses indicated that it was a mixture of anhydrous and hydrated salts, and no very definite numbers were obtained. No organic salts could be isolated.

4:7-Dinitro-6-hydroxy-1-phenyl-2-methyl-3-ethylbenziminazolol.

The red iminazolium hydroxide was dissolved in a warm solution of dilute sodium hydroxide, and the solution then acidified with hydrochloric acid. The carbinol is precipitated as a non-basic, microcrystalline, ochreous powder:

0.1086 gave 0.2128 CO_2 and 0.0448 H_2O . $\text{C}=53.44$; $\text{H}=4.59$.

0.0816 (air-dried) gave 10.9 c.c. N_2 (moist) at 16° and 752.8 mm.
 $\text{N}=15.42$.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_4$ requires $\text{N}=15.42$; $\text{C}=53.3$; $\text{H}=4.48$ per cent.

The carbinol is somewhat more orange in colour than the corresponding methyl derivative; its decomposing point is $250-252^\circ$. The most interesting character of this carbinol is its ready convertibility into the iminazolium form, and through the latter into the iminazolone. From this it appears that an increase in weight in the radicle attached to the 3-N-atom facilitates the isomeric change from the carbinol to the ammonium type. Thus, whilst the corresponding carbinol containing methyl requires prolonged boiling with water or alcohol to bring about the transformation, the present compound requires only a few minutes' boiling with alcohol to convert it into the red iminazolium hydroxide. The change even takes place in the dry substance on heating, a fact which was first brought under our notice by our observing that the ochreous carbinol, when dried at 100° , gradually became redder. A specimen dried at 110° until constant in weight became reddish-brown in colour, and gave the following results:

0.6252 (air-dried) lost, at 110° , 0.0346 $\text{H}_2\text{O}=5.5$ per cent.

0.0776 (dried at 110°) gave 10.75 c.c. N_2 (moist) at 13.5° and 758 mm. $\text{N}=16.29$.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_4-\text{H}_2\text{O}$ requires a loss $=5.0$ per cent.

$\text{C}_{16}\text{H}_{14}\text{O}_5\text{N}_4$ requires $\text{N}=16.37$ per cent.

The conversion of the dry substance into the iminazolone was thus complete, although the loss of water was somewhat in excess of that required by theory. The product was, however, contaminated with a small quantity of some secondary product of decomposition, as shown by its darker colour and by its leaving a slight residue on dissolving it in dilute acid. The acid extract after filtration and on neutralisation with ammonia gave the pure imin-

azolium hydroxide. The carbinol is also converted into the iminazolium form by boiling with glacial acetic acid.

4:7-Dinitro-6-hydroxy-1-p-tolyl-2:3-dimethylbenziminazolium Iodide and Hydroxide.

The iminazole from *p*-toluidine (Meldola and Hay, *Trans.*, 1908, **93**, 1673) was methylated by heating with excess of methyl iodide in a sealed tube for four hours at 130°. The product consisted of a mixture of dark and light ochreous, crystalline nodules, which proved to be the same compound, and of which the analysis indicated that complete methylation had taken place:

0.0927 gave 9.55 c.c. N₂ (moist) at 14° and 760.4 mm. N=12.13.

C₁₆H₁₅O₅N₄I requires N=11.91 per cent.

The substitution of *p*-tolyl for phenyl at the 1-N-atom has a marked influence on the stability of this iminazolium iodide, since, unlike the corresponding phenyliminazolium iodide, it is not decomposed by boiling with water. In order to isolate the iminazolium hydroxide in this case it was found necessary to boil the iodide with dilute hydrochloric acid. The more soluble iminazolium chloride is formed by this treatment, and the solution, after filtration to remove impurities and unmethylated iminazole, on neutralisation with ammonia deposits the iminazolium hydroxide in minute, ochreous scales. The compound is distinctly basic, dissolving readily in dilute mineral acids, and being precipitated unchanged on neutralisation; it is practically insoluble in alcohol, and but very sparingly soluble in boiling water. The decomposing point is above 300°. The air-dried substance was analysed:

0.0874 gave 0.1694 CO₂ and 0.0378 H₂O. C=53.02; H=4.80.

0.0882 „ 11.6 c.c. N₂ (moist) at 15° and 760.3 mm. N=15.4.

C₁₆H₁₆O₆N₄ requires C=53.3; H=4.48; N=15.55 per cent.

The marked difference in colour between this and the corresponding phenyliminazolium hydroxide, which is red, has already been pointed out. The present compound differs also from its homologue in the readiness with which it loses water and passes into the iminazolone.

4:7-Dinitro-6-hydroxy-1-p-tolyl-2:3-dimethylbenziminazolone.

The iminazolium hydroxide on exposure to the air for some days was found to have lost water, and to have become transformed into the above compound without undergoing any change in appearance, the iminazolone being also a microcrystalline, ochreous substance. The transformation takes place also under a desiccator,

and more rapidly when the hydroxide is heated. A specimen dried first under a desiccator and then at 130° until constant in weight gave the following result:

0.0812 gave 11.35 c.c. N_2 (moist) at 13° and 751.7 mm. $N=16.33$.

$C_{16}H_{14}O_5N_4$ requires $N=16.37$ per cent.

The iminazolone differs further from its lower homologue in its stability when once formed; it does not take up water on exposure to moist air, and can only be reconverted into the hydroxide base by dissolving it in dilute acid and reprecipitating by neutralising the solution. Four days' exposure to the air at the ordinary temperature are sufficient to reconvert it into the quinone-imide, as shown by a series of successive analyses.

Of the iminazolium salts of this series the *chloride* was prepared by dissolving the iminazolium hydroxide (or iminazolone) in alcohol saturated with hydrogen chloride, and adding an equal volume of ether, when the salt is precipitated as a white, microcrystalline powder, having a decomposing point of about $254-256^{\circ}$:

0.2536 gave 0.0935 AgCl. $Cl=9.03$.

0.1270 „ 15.8 c.c. N_2 (moist) at 15° and 754.2 mm. $N=14.45$.

$C_{16}H_{15}O_5N_4Cl$ requires $Cl=9.36$; $N=14.8$ per cent.

The hydroxide when boiled in alcoholic solution with picric acid forms a *picrate*, which crystallises in pale yellow needles, melting at 176° . The salt could not be purified by crystallisation from alcohol or any other solvent, as it is stable only in presence of excess of picric acid, and dissociates when heated in alcoholic solution.

4:7-Dinitro-6-hydroxy-1-p-tolyl-2:3-dimethylbenziminazolol.

The transformation of the iminazolium hydroxide is readily brought about by dissolving this compound in warm dilute alkali hydroxide, and adding hydrochloric acid to the orange-coloured solution, when the carbinol is precipitated as an ochreous, microcrystalline powder, indistinguishable in appearance from the iminazolium hydroxide, but devoid of basic properties, and distinctly phenolic in character. The decomposing point is above 300° :

0.1162 gave 0.2265 CO_2 and 0.0488 H_2O . $C=53.16$; $H=4.66$.

0.0884 „ 11.65 c.c. N_2 (moist) at 16° and 768.2 mm. $N=15.53$.

$C_{16}H_{16}O_4N_6$ requires $C=53.3$; $H=4.48$; $N=15.55$ per cent.

The carbinol is convertible into the iminazolium hydroxide form by the methods previously described.

Attempts to prepare the ethiodide of the *p*-tolyliminazole gave unsatisfactory results; the action of ethyl iodide at 130° is destructive, and at 115° no ethiodide is formed. At 120° some ethiodide

is formed, but is largely contaminated with tarry products of decomposition, and the iminazolium chloride itself appears to be easily resinised, so the experiments in this direction were discontinued.

We have pleasure in acknowledging the assistance rendered in the course of this research by Mr. S. G. Clifford, a former student of the Finsbury Technical College. We have also to express our indebtedness to the Government Grant Committee of the Royal Society, from which we have received a contribution towards the expenses incurred in carrying out the necessary experiments.

FINSBURY TECHNICAL COLLEGE.

CXLI.—*The Action of Salt Solutions and of Sea-water on Iron at Various Temperatures.*

By JOHN ALBERT NEWTON FRIEND and JOSEPH HALLAM BROWN.

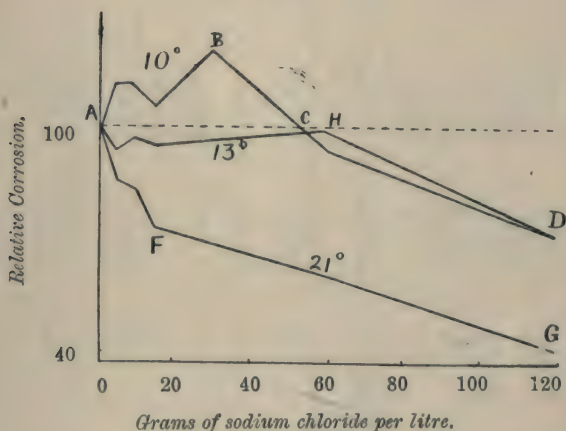
UNTIL comparatively recently our knowledge of the action of various concentrations of different electrolytic solutions on iron was of a purely qualitative nature. In 1908, Heyn and Bauer (*Mitt. Königl. Materialprüfungsamt*, 1908, 26, 2) published a monumental research on the subject, in which they showed that electrolytes may be divided into two classes, according as their concentrated aqueous solutions entirely prevent or merely partly retard the corrosion of iron immersed in them. By far the larger number of electrolytes belong to the second group, and the curve *ABCD* (Fig. 1) represents a typical case. *B* is the critical concentration, the corrosion being at a maximum, the point *A* representing the loss in weight of iron exposed to distilled water under otherwise exactly similar conditions. The reduced corrosive activity of the solution between *C* and *D* is attributable to the decreased solubility of the oxygen in the more concentrated solutions, an explanation which was first advanced by Adie (*Min. Proc. Inst. C. E.*, 1845, 4, 323) in the case of sodium chloride solutions.

For the chlorides and sulphates of the alkali metals, however, Heyn and Bauer obtained results indicated by the curve *AFG* (Fig. 1); that is, solutions of these salts were always less corrosive than fresh water at the same temperature.

As this result is contrary to the observations of numerous chemists (see Moody, *Proc.*, 1903, 157, 239; Mugdan, *Zeitsch. Elektrochem.*,

1903, 9, 442; Lindet, *Compt. rend.*, 1904, 139, 859; Cribb and Arnaud, *Analyst*, 1905, 30, 225), we thought it desirable to investigate the whole question, and determine, if possible, the reason for this anomaly. At first we exposed plates of Kahlbaum's pure iron foil, measuring 5×4 cm. in area, to solutions of the sulphates and chlorides of potassium and sodium. The plates were introduced into beakers (one plate in each beaker) in such a manner that their four corners rested in contact with the sides and bottom of the beaker, and were covered with 100 c.c. of solution. The beakers were then loosely covered with a bell-jar to prevent access of dust, but so arranged as to allow free passage of air. Precautions were likewise taken to prevent unequal illumination. After a period of fourteen days the plates were removed, cleaned, and weighed, the loss in weight being

FIG. 1.



taken as a measure of the corrosion. In every case on drawing the curve for the results, the form resembled that of *ABCD*.

Heyn and Bauer's experiments were carried out at a temperature between 18° and 22° , whereas our work was performed at a somewhat lower temperature. Although it seemed scarcely likely that such small differences in temperature should account for the lack of agreement between their results and ours, we carried out numerous series of experiments at various temperatures, the beakers being immersed in large thermostats specially designed for the purpose. The results of a few of the experiments with sodium chloride solutions are given in table I and shown graphically in Fig. 1, in which the loss in weight of the iron in pure water is taken as 100 at each temperature, the losses experienced by the other plates being expressed accordingly.

TABLE I.—*The Action of Solutions of Sodium Chloride on Iron at Various Temperatures.*

Temp. of Experiment.	10°.				13°.				21°.			
	Conc. of NaCl, grams per litre.	Initial wt. of iron, grams.	Loss in weight, gram.	Relative corrosion.	Initial wt. of iron, grams.	Loss in weight, gram.	Relative corrosion.	Initial wt. of iron, grams.	Loss in weight, gram.	Relative corrosion.	Initial wt. of iron, grams.	Loss in weight, gram.
	0	3.3492	0.0372	100	3.5702	0.0542	100	3.8724	0.1362	100	3.8724	0.1362
	0	3.4500	0.0378		3.5636	0.0540		3.8766	0.1168	86	3.8766	0.1168
	5	3.3758	0.0418	111	3.5654	0.0506	93	3.8996	0.1138	84	3.8996	0.1138
	10	3.3337	0.0411	110	3.6254	0.0512	97	3.5882	0.1010	74	3.5882	0.1010
	15	3.4258	0.0394	105	3.4744	0.0516	95	3.4074	0.0936	68	3.4074	0.0936
	30	3.4538	0.0450	120	3.5004	0.0518	96	3.5710	0.0836	61	3.5710	0.0836
	60	3.4568	0.0352	94	3.6400	0.0532	98	3.6300	0.0554	40	3.6300	0.0554
	120	3.5188	0.0272	72	3.6278	0.0390	72					

TABLE II.—*The Action of Various Concentrations of Sea-water on Iron at Various Temperatures.*

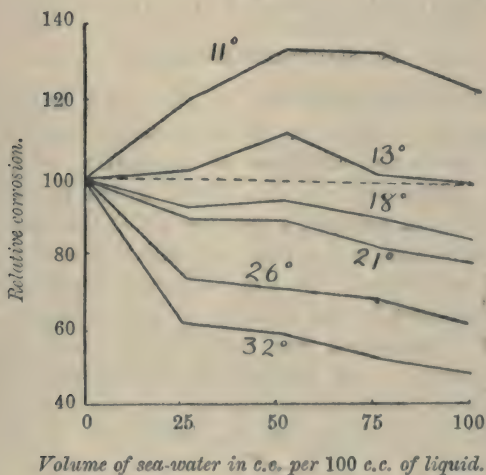
Liquid used, c.c.

Liquid used, c.c.	11°.				13°.				18°.			
	100 D*	100 D	75 D } 25 S†	50 D } 50 S }	25 D } 75 S }	100 S	100 D	100 D	75 D } 25 S†	50 D } 50 S }	25 D } 75 S }	100 S
	3.3684	0.0400	100	3.5072	0.0542	100	3.6658	0.0904	100	3.6658	0.0904	100
	3.5468	0.0402		3.5636	0.0540		3.4524	0.0902		3.4524	0.0902	
	3.5710	0.0486	122	3.4506	0.0554	103	3.4008	0.0831	92	3.4008	0.0831	92
	3.2938	0.0534	134	3.4980	0.0612	113	3.5558	0.0858	95	3.5558	0.0858	95
	3.4874	0.0534	134	3.5414	0.0556	103	3.7110	0.0820	91	3.7110	0.0820	91
	3.6480	0.0484	121	3.5616	0.0550	101	3.5578	0.0772	86	3.5578	0.0772	86
		21°.			26°.			32°.				
	3.5618	0.1084	100	3.4904	0.1392	100	3.4688	0.2332	100	3.4688	0.2332	100
	3.5164	0.1082		3.5436	0.1644		3.6934	0.2380		3.6934	0.2380	
	3.6160	0.0964	89	3.6702	0.1120	74	3.6084	0.1472	62	3.6084	0.1472	62
	3.4994	0.0974	90	3.6124	0.1018	67	3.5872	0.1404	60	3.5872	0.1404	60
	3.5496	0.0904	83	3.7674	0.1074	70	3.6244	0.1296	52	3.6244	0.1296	52
	3.5164	0.0872	80	2.8400	0.0866	64	3.5826	0.1224	45	3.5826	0.1224	45

From this we see that at temperatures above 13° , salt solutions of all concentrations exert a less corrosive action than fresh water at the same temperature, as indicated by curve *AFG*, but below this temperature the more dilute solutions are considerably more corrosive than fresh water, as indicated by the curve *ABCD*. At 13° dilute solutions of salt were practically equally as corrosive as distilled water, as indicated by *AH*. This temperature we propose to term the *Inversion Temperature*. The practical importance of these results is obviously very great, particularly in this country, where natural waters are usually at a lower temperature than 13° .

Now since sea-water contains a large proportion of sodium chloride,

FIG. 2.



it was important to determine whether or not its relative corrosive action is similarly influenced by changes of temperature.

To this end, pieces of pure iron, similar in all respects to those previously used, were exposed in a precisely similar manner to the action of distilled water, sea-water, and mixtures of the two in varying proportions. The results obtained are given in table II, and shown graphically in Fig. 2.

We thus see that at 13° the corrosive action of sea-water is the same as that of fresh water, but diluted sea-water is more corrosive than either. At lower temperatures the relative corrosivity of sea-water, both pure and dilute, is considerably enhanced, but at higher temperatures the addition of sea-water to fresh water renders the latter less corrosive. The results are of particular importance to

naval and marine engineers, and further experiments are in progress with the view of throwing further light on these curious phenomena.

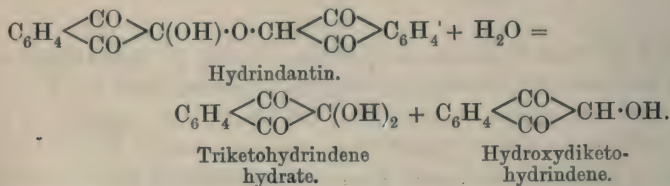
In conclusion, we have pleasure in acknowledging the kindness of the Research Fund Committee for a grant which is enabling us to carry out those experiments.

THE TECHNICAL COLLEGE, DARINGTON.

CXLII.—*Triketohydrindene Hydrate. Part IV.* *Hydrindantin and its Analogues.*

By SIEGFRIED RUHEMANN.

IT was recently shown (this vol., p. 792) that triketohydrindene hydrate resembles alloxan in its behaviour towards hydrogen sulphide, and yields the analogue of alloxantin, which was called hydrindantin. Attention was also drawn to the production of two different sodium salts, namely, a red one which the compound yields with sodium carbonate, and a blue salt which it forms with sodium hydroxide. The existence of two different chromo-salts cannot, however, be explained by the formula of hydrindantin. A further study of this phenomenon has revealed the fact that the blue metallic compound is not derived from hydrindantin, but is a salt of 2-hydroxy-1:3-diketohydrindene, and that the formation of the chromo-salt is preceded by the hydrolysis of hydrindantin, thus:



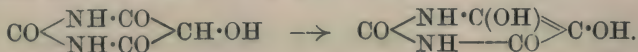
This explanation of the reaction is based on the following results. The blue solution of hydrindantin in sodium hydroxide, when kept for a short time, no longer contains hydrindantin, because, on the addition of hydrochloric acid, the colour disappears, but no solid is precipitated; hydrindantin, however, is produced on mixing the acid solution with triketohydrindene hydrate, dissolved in water. This behaviour is due to the change which, under the influence of the alkali, the triketone undergoes to *o*-carboxymandelic acid

(Trans., 1910, **97**, 2025). Hydroxydiketohydrindene, which is readily formed on reduction of the triketone, could not be obtained pure owing to the ease with which it is oxidised to hydrindantin; the fact, however, that it is very soluble in cold water rendered it possible to supply further evidence in support of the explanation of the colour reaction of hydrindantin. The aqueous solution of hydroxydiketohydrindene with sodium hydroxide at once yields a deep blue coloration, and with baryta a blue precipitate; it further forms hydrindantin on treatment with triketohydrindene hydrate. The formation of the chromo-salts may be explained in the simplest way by the change of hydroxydiketohydrindene into its tautomeric form, thus:

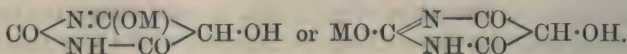


The red colour with which hydrindantin dissolves in sodium carbonate is most probably due to the formation of a salt of hydrindantin, because this compound is precipitated on the addition of mineral acids to the solution.

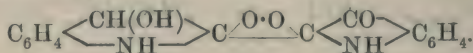
Since alloxantin closely resembles hydrindantin in the mode of formation and in its properties, the conclusion is justified that the violet barium compound which it yields with baryta is not a salt of alloxantin, but a chromo-salt of dialuric acid, the formation of which is preceded by the hydrolysis of alloxantin to alloxan and dialuric acid. That this acid forms a chromo-salt with baryta is indicated by Baeyer's statement (*Annalen*, 1863, **127**, 12), according to which the acid he obtained on reduction of alloxan or alloxantin always gave the colour reaction; and Friedrich (*Annalen*, 1906, **344**, 8) has pointed out that it occurs both with alloxantin and dialuric acid. A violet coloration is also produced on adding crystals of dialuric acid to a concentrated solution of sodium hydroxide, but the colour rapidly disappears. This behaviour is similar to that of isatin and the diketopyrrolines: these compounds, with the alkali, give a transitory violet or blue coloration previous to the fission of the pyrroline ring. A similar transformation may be expected to occur subsequently to the production of the coloured salt of dialuric acid, since, under the influence of alkalis, the pyrimidine ring readily ruptures, as, for instance, with alloxan and methyluracil. The reason why the violet barium compound of dialuric acid is more stable may be found in the less energetic action of baryta and in the insolubility of the chromo-salt. Its formation is undoubtedly accompanied (as in the former case) by the tautomeric change of dialuric acid, thus:



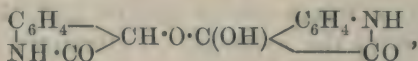
The colourless salts of this acid, which Friedrich (*loc. cit.*) proved to have the formula $MC_4H_3N_2O_4$, accordingly must be represented thus:



In close relation to alloxantin and hydrindantin stands isatide. This connexion is indicated by the following facts. Isatide is colourless; it is formed on reduction of isatin in acid solutions, as well as by the union of equal molecules of dioxindole and isatin; it is decomposed by dilute alkalis, and yields isatin on the addition of mineral acids to the alkaline solutions. Heller (*Ber.*, 1904, **37**, 946) considered isatide to have the constitution:



This formula, however, cannot be correct, for, on the one hand, it would lead to the conclusion that the compound is oxidised as readily as dioxindole, and on the other, it does not account for the ease with which isatide is decomposed by alkalis into dioxindole and isatin. The behaviour of the substance, however, is satisfactorily explained by the formula:



which corresponds with the one suggested by Piloty and Finckh and by Slimmer and Stieglitz for alloxantin. Of interest in this direction is the property of dioxindole of yielding a violet barium compound which gradually changes into a colourless salt (Heller, *loc. cit.*), because this fact may be regarded as a further support of the conclusions concerning the nature of the action of baryta on alloxantin.

Since alloxantin, hydrindantin, and isatide are formed from dialuric acid and alloxan, or the analogues of these compounds, it was to be expected that similar substances would be produced by the combination of the di- or tri-ketone of one series with the ketonic-alcoholic compound of another. As yet, only the behaviour of dialuric acid towards triketohydrindene hydrate has been examined, with the result that, instead of a union taking place, dialuric acid reduces the triketone and transforms it into hydrindantin. Experiments have also been made with the view of preparing the analogue of uramil, namely, 1:3-diketo-2-hydrindamine, $C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} CH \cdot NH_2$, from 2-oximino-1:3-diketo-hydrindene, $C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} C:NOH$. It was anticipated that this substance would

be reduced by hydriodic acid to the amine. The haloid acid, indeed, acts on the oximino-compound with the development of much heat, but effects the complete elimination of the nitrogen, and yields hydrindantin, which, by this method, is readily procurable. As will be shown in a subsequent paper, the transformation of oximino-diketohydrindene into the amine can be accomplished by using a solution of stannous chloride in hydrochloric acid, instead of hydriodic acid.

EXPERIMENTAL.

Formation of 2-Hydroxy-1:3-diketohydrindene.

Triketohydrindene hydrate is readily reduced to the analogue of dialuric acid by sodium amalgam. On adding the amalgam ($2\frac{1}{2}$ per cent.) to the concentrated aqueous solution of the triketone, a deep blue coloration is produced, which does not disappear under the influence of an excess of the amalgam. The alkaline solution, when acidified with dilute hydrochloric acid, loses its colour, but no solid separates. The presence of hydroxydiketohydrindene is indicated by the disappearance of the blue colour of the alkaline liquor when oxygen is passed into it, and its formation is proved by the production of the insoluble hydrindantin on treatment of the acid solution with triketohydrindene hydrate. As a convenient solvent for the extraction of the hydroxydiketone from the solution could not be found, an attempt was made to effect its isolation by using stannous chloride for the reduction of the triketone. For this purpose a hot solution of tin (4 grams) in concentrated hydrochloric acid was added to triketohydrindene hydrate (2 grams), dissolved in a little boiling water; hydrindantin was immediately precipitated, but redissolved on digesting the mixture on the water-bath. The yellowish-red solution was then freed from tin by hydrogen sulphide, and the filtrate from the metallic sulphide evaporated in a vacuum at 45—50°. The residue readily dissolved in water, with the exception of a small quantity of hydrindantin, which was formed during the process. This was removed by filtration, and the clear liquid placed into a vacuum desiccator over sulphuric acid; but, although all the operations were carried out as rapidly as possible, partial oxidation to hydrindantin could not be avoided. Owing to this circumstance, further attempts to isolate hydroxydiketohydrindene and to verify its composition by analysis had to be abandoned, but its presence in the solution could readily be ascertained by the same reactions which, in the former case, served for its identification.

Action of Dialuric Acid on Triketohydrindene Hydrate.

On dissolving dialuric acid (1 gram) in hot water which previously had been freed from air by boiling, and adding an aqueous solution of triketohydrindene hydrate (1.2 gram), colourless crystals separate when the mixture is heated for a short time. The solid (0.9 gram) does not contain nitrogen, and was identified with hydrindantin by its reactions and by analysis of the substance after recrystallisation from acetone, and drying it in the water-oven. (Found, $C=67.07$; $H=3.21$. Calc., $C=67.08$; $H=3.10$ per cent.) It follows, therefore, that the triketone is almost completely reduced by dialuric acid to hydrindantin.

Formation of Hydrindantin from 2-Oximino-1:3-diketohydrindene.

The oximino-compound, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} > C:NOH$, is readily prepared by the action of nitrous acid on 1:3-diketohydrindene (W. Wislicenus, *Annalen*, 1888, **246**, 353). On adding fuming hydriodic acid to the crystals, an energetic action takes place; heat is developed, iodine separates, and, finally, the whole sets to a semi-solid. This is suspended in water, and the halogen removed by sulphurous acid, when a light brown substance is left behind, which is collected and dried in a vacuum desiccator. It is free from nitrogen, almost insoluble in water, crystallises from acetone in colourless prisms, and dissolves in sodium hydroxide to yield a blue solution. These properties, together with the analysis, characterise the compound as hydrindantin. (Found, $C=67.03$; $H=3.17$. Calc., $C=67.08$; $H=3.10$ per cent.)

Fuming hydriodic acid, therefore, hydrolyses the oximino-compound, and transforms it into triketohydrindene hydrate, which is subsequently reduced to hydrindantin. Such a change, however, does not occur on using stannous chloride instead of hydriodic acid for the reduction of the triketone, which is thus transformed into diketohydrindamine. A detailed account of the properties of this compound will be published shortly.

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